PB90-226820

Pesticide Spray Penetration and Thermal Comfort of Protective Apparel for Pesticide Applicators

Tennessee Univ., Knoxville

Prepared for:

Environmental Protection Agency, Cincinnati, OH

Jun 90

U.S. Department of Commerce
National Technical Information Service
NTIS

PB90-226820

EPA/600/2-90/023
June 1990

PESTICIDE SPRAY PENETRATION AND THERMAL COMFORT OF PROTECTIVE APPAREL FOR PESTICIDE APPLICATORS

by

Jacquelyn O. DeJonge
The University of Tennessee
Knoxville, Tennessee 37996-1900

and

Elizabeth Easter
University of Kentucky
Lexington, Kentucky 40506

Cooperative Agreement No. 812486-01-0

Project Officer

S. Krishnamurthy
Releases Control Branch
Superfund Technology Demonstration Division
Risk Reduction Engineering Laboratory
Edison, New Jersey 08837

RISK REDUCTION ENGINEERING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA/600/2-90/023

2.

3. RECIPIENT'S ACCESSION NO.
PB90 226820/AS

4. TITLE AND SUBTITLE
Pesticide Spray Penetration and Thermal Comfort of Protective Apparel for Pesticide Applicators

5. REPORT DATE

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Jacquelyn O. DeJonge and Elizabeth Easter

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
The University of Tennessee
110 Jessie Harris Building
Knoxville, TN 37996-1900

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Risk Reduction Engineering Laboratory--Cincinnati, OH
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

13. TYPE OF REPORT AND PERIOD COVERED
Proj. Report 10/1/85-1/31/89

14. SPONSORING AGENCY CODE
EPA/600/14

15. SUPPLEMENTARY NOTES
Project Officer: S. Krishnamurthy (201) 321-6796 FTS 684-6796

16. ABSTRACT

The use of protective apparel to serve as a barrier from dermal exposure is considered vital for providing some measure of protection for those who work with and around pesticides. This research is aimed at ultimately providing recommendations for types of protective apparel for pesticide application for dermal exposure protection and thermal comfort.

A laboratory spray system was developed and validated that delivers a controlled amount of pesticide solution to fabric samples for pesticide penetration evaluation. Woven fabrics of varying thickness and weight were evaluated. When thickness remained the same, pesticide spray penetration could be attributed to weight. As fabric weight increased, pesticide penetration decreased. Wearing clothing with fabric weight below 250 g/m^2 (7.37 oz/yd^2) is not recommended.
sq m sq yd

Laboratory evaluation of nonwoven fabrics found alternatives to the most commonly used nonwoven fabric (Tyvek), all providing equally good protection. A screening of fabrics for thermal comfort determined that plain weave, light weight, woven fabrics were the most comfortable. Of the nonwoven fabrics evaluated, the combination of polyester and wood pulp showed the best promise as comfortable protective apparel.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pesticides Human Environmental Effects	Apparel Clothing	

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
157

22. PRICE

EPA Form 2220-1 (9-73)

8

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Cooperative Agreement No. CR 812486-01-0 to The University of Tennessee, Knoxville. It has been subject to the Agency's peer and administrative review and it has been approved as an EPA final report. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This document contains information on the use of protective apparel as a barrier from dermal exposure to pesticides. It describes a laboratory spray system that simulates a field application and can serve as a screening of the barrier properties of fabrics. The information is intended for supporting OPP decisions in the areas of agricultural protective clothing regulations, pesticide registration, training programs, and technical assistance.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

The use of protective apparel to serve as a barrier from dermal exposure is considered vital for providing some measure of protection for those who work with and around pesticides. This research is aimed at ultimately providing recommendations for types of protective apparel for pesticide application for dermal exposure protection and thermal comfort.

A laboratory spray system was developed and validated that delivers a controlled amount of pesticide solution to fabric samples for pesticide penetration evaluation. Initial penetration evaluation of fabrics currently used by agricultural workers determined that fabrics of different construction and fiber content provide varying degrees of protection. Fabric characteristics of thickness, air permeability, weight, finish and fiber content may be valuable indicators of fabric penetration performance. Further isolation of fabric characteristic variables was necessary to clarify the confounding variables. Woven fabrics of varying thicknesses and weight were evaluated. When thickness remained the same, pesticide penetration could be attributed to weight. As fabric weight increased, pesticide penetration decreased. Based on the laboratory penetration data generated in this study it is recommended that agricultural workers exposed to pesticide sprays should not wear clothing of woven fabrics weighing less than 250 g/m^2 (7.37 oz/yd^2).

Laboratory pesticide penetration evaluation of nonwoven fabrics found several alternatives to the most commonly used nonwoven fabric all providing equally good protection. The application of pressure and contamination at higher levels increased the severity of laboratory spray testing and is recommended to evaluate fabric performance for a worst case senario. The evaluation of seams and zippers validated the importance of placement on the garment because of altered pesticide penetration through fabric in seam or closure area.

A screening of fabrics for thermal comfort determined that a battery of three laboratory tests differentiated thermal ratings of fabrics. Plain weave, light weight woven fabrics, which offer no protection against pesticide penetration, were rated as the most comfortable based on the laboratory data. Of the nonwoven fabrics evaluated, the combination of polyester and wood pulp showed the best promise as comfortable protective apparel.

This final report covers the period October 1, 1985 through January 31, 1989.

TABLE OF CONTENTS

Page

Disclaimer ii
Foreword iii
Abstract iv
Tables vi
Figures ix
Acknowledgements xii
1. Introduction 1
2. Conclusions 2
3. Recommendations 4
4. Penetration Test Method 5
5. Pesticide Penetration Through Fabrics 16
6. Thermal Comfort Assessment 98
References 108

Appendices

A. Standard Operating Procedures 111
B. High Performance Liquid Chromatograph Conditions 118
C. Quality Assurance 120

TABLES

Page

1 RATE OF NOZZLE MOVEMENT AT EACH DIAL SETTING 9
2 SPRAY CHAMBER VALIDATION: LIQUID DELIVERY 10
3 PRESSURE'S EFFECT ON DROPLET SIZE & DISTRIBUTION 11
4 EFFECT OF SEPARATION BETWEEN FABRIC AND NOZZLE 14
5 FABRIC DESCRIPTIONS: INITIAL STUDY 17
6 FABRIC CHARACTERISTICS: INITIAL STUDY 17
7 ANALYSIS OF VARIANCE: INITIAL STUDY 19
8 PESTICIDE PENETRATION: INITIAL STUDY 20
9 DUNCAN'S MULTIPLE RANGE TEST: INITIAL STUDY 21
10 GENERAL LINEAR MODEL: INITIAL STUDY 37
11 FABRIC DESCRIPTION: WEIGHT & THICKNESS STUDY 41
12 CHARACTERISTICS OF WOVEN FABRICS 42
13 PESTICIDE PENETRATION THROUGH WOVEN FABRICS 45
14 DUNCAN'S MULTIPLE RANGE TEST -CHLOROBENZILATE 48
15 DUNCAN'S MULTIPLE RANGE TEST - ETHION 49
16 DUNCAN'S MULTIPLE RANGE TEST - DICOFOL 50
17 FABRIC DESCRIPTIONS: NONWOVEN STUDY 57
18 PESTICIDE PENETRATION THROUGH NONWOVEN FABRICS 57
19 DUNCAN'S MULTIPLE RANGE TEST - CHLOROBENZILATE 59
20 DUNCAN'S MULTIPLE RANGE TEST - DICOFOL 60
21 DUNCAN'S MULTIPLE RANGE TEST - ETHION 61
22 FABRIC DESCRIPTIONS: PRELIMINARY PRESSURE STUDY 64
23 PESTICIDE PENETRATION: PRELIMINARY PRESSURE STUDY 66
24 FABRIC CHARACTERISTICS: PRESSURE STUDY 67
25 CAPILLARY PENETRATION - DICOFOL 69
26 PRESSURE PENETRATION - DICOFOL 69

TABLES (continued)

Page

27 ANALYSIS OF VARIANCE: DICOFOL PENETRATION 70
28 ANALYSIS OF VARIANCE:DICOFOL CONTAMINATION LEVEL 70
29 ANALYSIS OF VARIANCE: DICOFOL PRESSURE 71
30 DUNCAN'S MULTIPLE RANGE TEST: PRESSURE STUDY 71
31 TERRAZOLE® PENETRATION 72
32 TERRAZOLE® PRESSURE PENETRATION STUDY 72
33 ANALYSIS OF VARIANCE TERRAZOLE® PENETRATION 73
34 SEAMS AND ZIPPERS DESCRIPTION 75
35 FABRIC DESCRIPTIONS: SEAMS AND ZIPPERS STUDY 75
36 FABRIC CHARACTERISTICS: SEAMS AND ZIPPERS STUDY 76
37 DICOFOL PENETRATION: SEAM STUDY 77
38 MEAN PERCENTAGE OF SEAMS FOR DICOFOL 78
39 ANALYSIS OF VARIANCE FOR DICOFOL SEAM STUDY 78
40 TERRAZOLE® PENETRATION: SEAM STUDY 79
41 ANALYSIS OF VARIANCE TERRAZOLE® SEAM STUDY 79
42 ORTHOGONAL CONTRAST ANALYSIS TERRAZOLE® SEAM 80
43 PERCENTAGE OF ZIPPERS WITH PENETRATION 81
44 ANALYSIS OF VARIANCE: DICOFOL ZIPPER STUDY 82
45 SIGNIFICANT LEVEL OF PROBABILITY BETWEEN ZIPPERS 82
46 THERMAL DIFFUSION LENGTHS COMPUTED FOR COTTON AND SMS AT 1000 CM-1 85
47 PEAK RATIOS - FTIR/PAS SPECTRA: COTTON 86
48 PEAK RATIOS - FTIR/PAS SPECTRA: FINISHED COTTON 92
49 PEAK RATIOS FTIR/PAS SPECTRA:SMS 97
50 FABRIC DESCRIPTIONS: THERMAL STUDY 99
51 HEAT STRESS RELIEF SCORE RANKINGS 106
52 TERRAZOLE® EXTRACTION EFFICIENCY 121

TABLES (continued)

Page

53 DICOFOL EXTRACTION EFFICIENCY 122
54 DICOFOL REINJECTION DATA-STANDARDS 123
55 TOTAL NUMBER OF SAMPLES WOVEN 130
56 TOTAL NUMBER OF SAMPLES NONWOVEN 131
57 TOTAL NUMBER OF SAMPLES SEAMS 132
58 TOTAL NUMBER OF SAMPLES ZIPPER CLOSURES 133
59 EPA PESTICIDE ANALYSIS-INTERLAB SPECIMEN I.D 134
60 EPA PESTICIDE ANALYSIS-INTERLAB TEST U.T HPLC 134
61 EPA PESTICIDE ANALYSIS-INTERLAB TEST U.T GC 135
62 SAMPLING DIAGRAM VARIABLES AFFECTING PENETRATION 135
63 SAMPLING DIAGRAM (EFFECT OF SEAMS - DICOFOL) 137
64 SAMPLING DIAGRAM (EVALUATION NONWOVEN FABRICS) 138
65 SAMPLING DIAGRAM (SEAMS -TERRAZOLE®) 138
66 SAMPLING DIAGRAM (ZIPPERS - DICOFOL) 139
67 SAMPLING DIAGRAM (PENETRATION - DICOFOL) 140
68 SAMPLING DIAGRAM (PENETRATION - TERRAZOLE ®) 141
69 SAMPLING DIAGRAM (FABRICS TERRAZOLE®) 142
70 SAMPLING DIAGRAM (FABRICS DICOFOL) 143
71 TOTAL CONTAMINATION LEVELS 144

FIGURES

Page

1 Illustration of Spray Chamber 6
2 Illustration of a Fabric Holder 7
3 Droplet Distribution at Varying Pressures 11
3 (continued) 12
3 (continued) 13
4 Illustration of MultiLayer Sample 18
5 Pesticide Amount Penetrated by Pesticide 22
6 Spray Rating vs Penetration by Pesticide 23
6 (continued) 24
7 Surface Energy vs Penetration by Pesticide 26
7 (continued) 27
8 Comparisons of Treated and Untreated Fabrics 28
8 (continued) 29
8 (continued) 30
9 Air Permeability vs Penetration by Pesticide 31
9 (continued) 32
10 Weight vs Penetration for Untreated Fabrics 35
10 (continued) 36
11 Woven Fabric Thickness 43
12 Woven Fabric Weight 43
13 Woven Fabrics Compared by Weight and Thickness 44
14 Fabric Pesticide Penetration - Chlorobenzilate 46
15 Fabric Pesticide Penetration - Dicofol 46
16 Fabric Pesticide Penetration - Ethion 47
17 Comparison of Pesticide Penetration 47
18 Duncan's Multiple Range Test - Chlorobenzilate 50

FIGURES (continued)

Page

19 Duncan's Multiple Range Test - Ethion 51

20 Duncan's Multiple Range Test - Dicofol..51

21 Regression Line Unfinished Fabric: Chlorobenzilate..................................53

22 Regression Line Unfinished Fabric: Dicofol..53

23 Regression Line Unfinished Fabric: Ethion...54

24 Pesticide Penetration through Nonwoven Fabric 58

25 Duncan's Multiple Range Test - Chlorobenzilate 59

26 Duncan's Multiple Range Test - Dicofol...60

27 Duncan's Multiple Range Test - Ethion 61

28 Ratio of Dicofol peak intensity to cotton peak intensity versus optical velocity for the fabric face..87

29 Ratio of Terrazole® peak intensity to cotton peak intensity versus optical velocity for the fabric face. 87

30 Plot of chlorine atomic concentration versus argon ion sputter time : diluted dicofol - cotton. 88

31 Plot of nitrogen, chlorine, and sulfur atomic concentrations versus argon ion sputter time: concentrated Terrazole® - cotton. 88

32 Plot of nitrogen, chlorine, and sulfur atomic concentrations versus argon ion sputter time : diluted Terrazole® - cotton. 89

33 Ratio of Dicofol peak intensity to finished cotton peak intensity versus optical velocity for fabric face. 90

34 Ratio of Terrazole® peak intensity to finished cotton peak intensity versus optical velocity for fabric face. 90

35 Plot of nitrogen, chlorine, and sulfur atomic concentrations versus argon ion sputter time: diluted Dicofol - finished cotton. 91

36 Plot of nitrogen, chlorine, and sulfur atomic concentrations versus argon ion sputter time: diluted Terrazole®- finished cotton.........................92

37 Ratio of Dicofol peak intensity to SMS peak intensity versus optical velocity for the fabric face...94

FIGURES (continued)

Page

38 Ratio of Terrazole® peak intensity to finished SMS peak intensity versus optical velocity for the fabric face. 94

39 Plot of chlorine atomic concentrations versus argon ion sputter time: diluted Dicofol - SMS. 95

40 Plot of nitrogen, chlorine, and sulfur atomic concentrations versus argon ion sputter time: concentrated Terrazole®-SMS. 95

41 Plot of chlorine, nitrogen, and sulfur atomic concentrations versus argon ion sputter time: dilute Terrazole ® - SMS. 96

42 Thermal Test Battery Results U-Value: Woven 102

43 Thermal Test Battery Results U-Value: Nonwovens 102

44 Thermal Test Battery Wind Penetration:Woven 103

45 Wind Penetration:Nonwovens 103

46 Thermal Test Battery Results CLORT: Woven 105

47 Thermal Test Battery Results CLORT: Nonwoven 105

48 Heat Stress Relief Scores 106

ACKNOWLEDGEMENTS

This project involved the combined efforts of faculty, graduate students, and technicians in the Textiles, Merchandising and Design Department at UTK. The work of the following individuals is represented in the research: Maria Anastasakis, Randy Bresee, John Crouse, Carol Dimit, Kermit Duckett, Charlie Hassenboehler, Karen Leonas and Katie Van Peursem.

In addition, the technical services of John Brother, Frank Calogero, Becky Layman, Bill Sanders and John Schneider provided assistance in the analysis.

Pat Shireman and Kurt Weiss are responsible for the preparation of this document.

SECTION 1

INTRODUCTION

The use of toxic chemicals in agricultural production is a major source of potential health risk. Previous research has shown that the main route of pesticide exposure is dermal rather than through the respiratory system. Therefore, the use of protective apparel as a barrier from dermal exposure is considered vital in providing some measure of protection for those who work with and around pesticides. To date, research on apparel as a protective barrier has identified some fabrics which allow minimal or no penetration of pesticide particulates. The research in this area has been conducted on isolated pesticides and fabrics with little consideration given to the variables in the pesticide formulation and fabric characteristics which may affect penetration. A systematic approach to defining the variables in both pesticides and fabric variations is needed in preparation for extensive testing of these variables to contribute toward a predictive model for pesticide penetration through fabrics.

Fabrics currently available which serve as a good protective barrier are considered thermally uncomfortable to wear. Various alternatives for fabric finishing to increase protection while maintaining reasonable thermal acceptance need to be examined. Ultimately this research is aimed at providing recommendations for types of protective apparel for pesticide applicators which will provide adequate dermal protection and will also minimize thermal discomfort. Such an investigation will be accomplished with two overall objectives:

1. The development of a predictive model to assess fabric penetration performance through:
    a. Validation of standardized penetration test method;
    b. Collection of penetration data on pesticide and fabric variables;
    c. Fabric characterization through physical testing and microscopy.
2. Laboratory screening of protective fabrics to assess thermal comfort parameters through:
    a. Heat transfer testing of fabrics with acceptable penetration performance;
    b. Fabric characterization through physical testing.

The specific objectives presented below and addressed in this report contribute to both of the overall objectives above:

1. Validation of a pesticide spray penetration test method;
2. Collection of pesticide spray penetration data using various pesticides and woven and nonwoven fabrics;
3. Analysis of pesticide spray penetration data;
4. Effect of fabric characteristics on pesticide penetration;
5. Effect of pressure and contamination level on pesticide penetration;
6. Effect of seams and closures on pesticide penetration;
7. Indepth profile of pesticide penetration into fibers and fabrics;
8. Thermal screening of fabrics through heat transfer testing.

SECTION 2

CONCLUSIONS

The research performed under this cooperative agreement involves developing and validating a laboratory spray method to test fabric penetration of pesticides, collecting data on spray penetration of pesticides through protective apparel fabrics, and evaluating the relationship between protective apparel fabric characteristics and thermal comfort. The following conclusions may be drawn:

1. A reproducible penetration test method applied controlled pesticide sprays to flat fabric swatches and measured the resultant penetration. This method can be used to screen fabrics for their ability to protect a pesticide applicator's covered skin from pesticide spray.
2. A database of laboratory spray penetration data and fabric characteristics was created for 18 woven fabrics and 10 nonwoven fabrics. Each woven fabric was characterized according to thickness, weight, air permeability, yarn count, and surface energy. Each nonwoven fabric was characterized according to fiber content and finish.

   a. The weight of woven fabrics most influenced their penetration resistance; as weight decreased, penetration increased.

   b. Nonwoven fabrics having a film finish were most resistant to pesticide spray penetration.
3. Clothing of woven fabrics weighing less than 250 g/m^2 (7.37 oz/yd$^{2)}$ is much less resistant to pesticide spray penetration than is clothing of heavier fabrics. Heavier fabrics, however, will not necessarily provide adequate protection.
4. The application of pressure and higher levels of contamination increased external pesticide penetration of the fabric.
5. Seams and zippers in a garment may increase the potential for pesticide penetration.
6. Pesticides were readily absorbed into cotton fabrics. This suggests that a layer of cotton fibers in protective apparel could possibly provide dermal protection through a mechanism involving absorption of pesticide into the fiber interior.
7. The fact that nonwoven composite fabric SMS retains the greatest amount of pesticide on the interior of the fabric structure suggests that a new generation of composite fabrics may help provide increased pesticide protection.

8. Thermal comfort of fabrics were ranked from tests to measure heat, moisture, and air transport.

   a. For the nonwoven fabrics, weight and thickness are inversely related to estimated thermal comfort.

   b. For the nonwoven fabrics, including a natural fiber, such as wood pulp, increased the estimated thermal comfort of the fabric.

SECTION 3

RECOMMENDATIONS

1. The spray chamber test method developed in this project should be used to screen fabrics for pesticide penetration performance before field evaluations.

2. The spray chamber test method should be evaluated for adoption as a standard American Society for Testing and Materials test method.

3. To insure statistically valid relative comparisons of data, chambray, Tyvek®, and SMS should be included in each successive experimental design.

4. The laboratory pesticide spray penetration database should be expanded by adding penetration data and fabric characteristics from laboratory and field evaluations of fabrics with novel materials or construction characteristics.

5. Agricultural workers exposed to pesticide sprays should be cautioned against wearing clothing of woven fabrics that is lighter in weight than 250 g/m^2 (7.37 oz/yd^2). Clothing may be either purchased with this weight or may decrease to this weight through use over time (e.g., old denim jeans).

6. Before concluding that fabrics above 250 g/m^2 will offer good spray penetration resistance, fabrics over 250 g/m^2 should be tested to evaluate the effect of movement of the body during wear, pesticide build-up on fabrics, and additional spray conditions.

7. Effective worst-case laboratory spray evaluation should include the application of pressure to the exposed fabric.

8. Seams in protective apparel should be used in moderation to limit additional pesticide exposure.

9. In areas of maximum pesticide absorption (scrotum), the lapped, traditional zipper rather then the commonly used open and centered zipper should be used in protective apparel.

SECTION 4

PENETRATION TEST METHOD

VALIDATION OF PENETRATION TEST METHOD

Three methods of fabric contamination are commonly used to evaluate a fabric as a barrier against pesticide penetration: field studies, drop methods, and laboratory spray systems. Field studies use actual field conditions and monitor the amount of pesticide that penetrates the garment or fabric. The penetrating pesticide is collected on gauze pads for analysis. Field studies are invaluable in ascertaining the acceptability of a garment, but they can be costly and time consuming. In addition, controlling variables that may influence penetration is difficult. These variables include droplet size, velocity, and environmental conditions, such as wind and sun. The total amount of pesticide one comes in contact with is difficult to determine, and thus makes reproducibility unlikely (1).

The drop method uses a pipette to apply a known amount of pesticide to the fabric (2) and provides for application of a controlled amount of pesticide in a reproducible manner; however, it more closely simulates mixing, cleaning up, and spill situations than application situations.

The third method of exposing fabrics to pesticide solutions is a laboratory spray system. Orlando et al. (3), used a Beltsville sprayer initially designed to spray vegetation. Its size made it cumbersome for fabric testing, and control of environmental conditions was difficult because it had to be housed in a large room. Easter (4) used a spray chamber in her studies designed to spray one fabric sample at a time. The sample was manually inserted into the chamber, exposed to a known amount of pesticide (based on time), and then removed. These spray systems were the prototype for the refined and expanded spray system discussed here.

This spray system design allows for monitoring the influence of droplet size, as in field studies, while controlling the amount of pesticide delivered to the fabric as in the drop method. The droplets, formed with a spray nozzle, more closely simulate the actual field condition of a pesticide spray impinging on the test fabric (5). The chamber can be housed in a laboratory hood, providing localized control of environmental conditions. The amount of pesticide that each fabric is exposed to is mechanically controlled.

Pesticide Spray Chamber Design

The equipment is designed for observing the spraying operation, operator protection, pesticide concentration and liquid flow rate control, and aerial distribution uniformity of liquid sprayed across the fabric sample. The integrated system consists of specific components: (a) spray chamber, (b) fabric sample holders, (c) spray nozzle and mechanical control, and (d) pesticide reservoir and liquid feed line.

The chamber housing is constructed in the form of a rectangular box from 1.2 cm thick clear plexiglass sheeting (Figure 1). The outside dimensions measure 115 cm long, 60 cm high, and 30 cm deep. Contacting edges are attached with a solvent contact adhesive, with the exception of the top plate. This plate is attached to the four sides with machine screws, thereby providing access to the interior in the event of necessary repair or top replacement. For the purpose of general cleaning and routine access to the inside of the chamber, two 20 cm diameter portholes have been machined into the front panel. These are fitted with circular plexiglass window panes, each held in place by frictional contact of an o-ring attached to the outside edge of the window pane and the edge surface of the porthole in the chamber. Handles on the panes provide for easy removal and replacement.

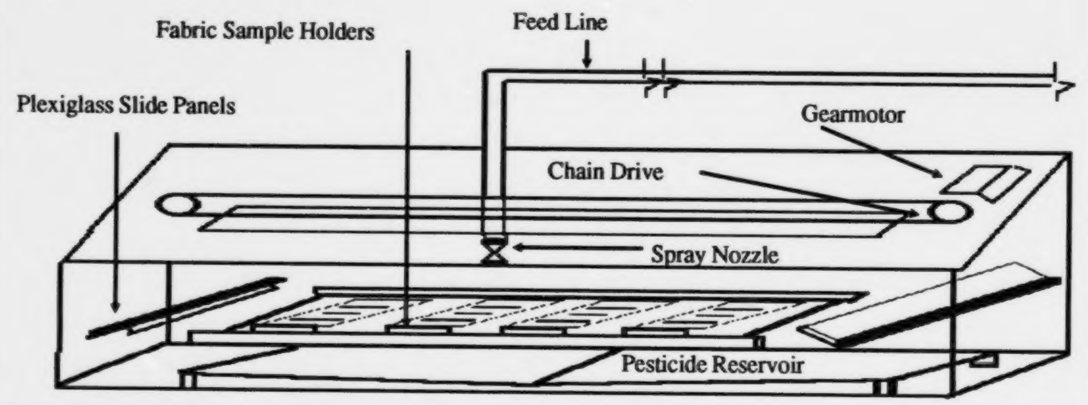


Figure 1. Illustration of Spray Chamber

The top plate also has a lengthwise slot through the middle to within about 10 cm of the ends. The slot width accommodates a stainless steel feed line to which is attached a spray nozzle directed downward into the chamber interior. The lengthwise slot provides clearance for a sweeping motion of the spray nozzle across fabric samples mounted beneath. Sample-nozzle separation distance adjustments are set by lowering or raising the stainless steel tubing to which the nozzle is attached. This tube, itself, passes through a matched hole drilled through a plexiglass block carriage constructed to ride on two stainless steel rods mounted above the top plate of the chamber and parallel to the open slot through which the spray head projects. Left and right carriage motion is handled by a positive-drive chain driven by a variable speed, reversible Dayton gearmotor. Appropriate electrical switching and voltage controls provide variable speeds of the nozzle and, hence, adjust the rate of pesticide coverage when used in conjunction with known rates of liquid volume feed. A sweeping spray can be obtained from either direction. The bottom of the chamber is configured with a v-shape geometry, which provides drainage to the center of the chamber where liquids are removed by gravity feed through a drain pipe into collector cans for appropriate, safe disposal. Plexiglass panels are mounted at each end of the chamber on the inside in a configuration that protects the fabric specimens from direct pesticide spray when the nozzles reach the end of their sweeping motions. Such a configuration allows the spraying to continue unabated, and eliminates variability in spraying rates that are present when starting and stopping the spray feed operation. The complete spray chamber unit is placed within a laboratory fume hood for obvious safety reasons associated with spraying toxic pesticides.

The fabric holders are similarly fabricated of 1.5 cm thick plexiglass in a tenter frame style with spring-loaded clamps to hold the fabric specimens in place and to aid in the ease of securing and removing fabric samples (Figure 2). A tenter frame is commonly used in textile processing to hold the fabric firmly at the edges, leaving the center area taut and unconstricted. The overall dimension of the holder are 37 cm long by 18 cm wide, with the sample area 12.8 cm by 12.8 cm. At the opposite end to the sample area is the handle, with a stop plate for setting the distance to which the fabric can be inserted through a slot milled in the front panel of the spray chamber. There are four slots in the front panel to accommodate four fabric holders. A plexiglass strip on the back, inside panel acts as a rest stop for each holder when set in place for a spray treatment. A splash guard is attached to the inside front panel above the slots to eliminate pesticide leakage during spraying.

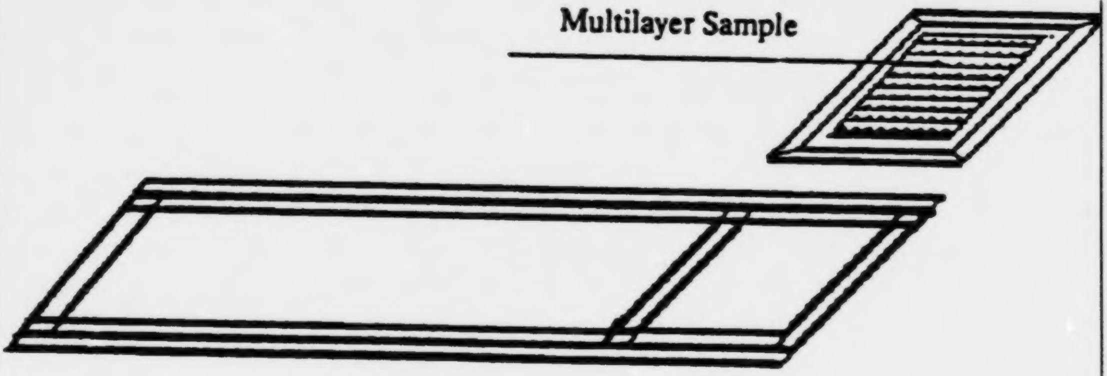


Figure 2. Illustration of a Fabric Holder

The pesticide solution is delivered from a two-liter polyethylene terephthalate bottle through a reinforced polyethylene standard spray hose. This 6 mm internal diameter (ID) hose is coupled with another flexible pneumatic hose of similar size connected to the nozzle tube that is fixed in the traveling carriage. The flexibility of the hose minimizes drag as the nozzle carriage traverses its sweep directions. Connections between hoses and other points in the feed line are made with Kwik Change® Connectors (Milton Couplet). The pesticide reservoir bottle rests on the plate surface of a magnetic stirrer, operated during spraying to provide a uniform, constant concentration of pesticide solution to the spray feed line. Helium gas, a chemically inert gas, is used to provide the driving pressure and is fed from a regulator controlled tank through a rubber hose to the space in the reservoir above the pesticide solution. The volume flow rate of solution delivered to the spray chamber is controlled by a combined choice of gas driving pressure and spray nozzle.

The nozzle is passed across the length of the chamber, above the fabric samples, by a motor mounted on the outside of the chamber. A control box, outside the chamber, is used to start and stop the motor, to change nozzle direction and to control the nozzle speed. The nozzle speed is adjusted by a variable dial allowing for settings from 0 (lowest) to 10 (highest).

Stop latches at each end of the chamber automatically shut the motor off when the nozzle reaches the end of the chamber. This allows for continued feed of the pesticide solution while removing or inserting fabric samples. Continuous spray of the pesticide solution ensures no fluctuation in pressure due to starting and stopping of the liquid flow.

The nozzle can be changed easily to allow for varying spray patterns and amounts of pesticide delivered. The distance between the nozzle tip and fabric sample is also adjustable ranging from 25.4 cm to 38.1 cm. The amount of total spray delivered to the sample depends on the choice of nozzle, the hydraulic driving pressure in the feed line at the nozzle, separation distance between the nozzle and the fabric, and the time interval over which the test fabric is subjected to spraying.

Calibration and Validation

The spray chamber has been evaluated using several different methods to ensure consistent and accurate spray application to each test specimen location. Spray coverage uniformity, consistency in the amount of liquid delivered, the effect of pressure on droplet size and the effect of separation distance between the nozzle and the test specimen location were evaluated.

To determine the uniformity of the spray (a well-dispersed pattern with equal amounts of liquid/particle solution striking all areas of the test specimen) a fluorescein dye solution (0.12%) was used in the chamber. This method was similar to one used by DeJonge et al. (5) and provided an orange-green solution by which to evaluate visually the spray pattern. A 130 g/m^2,100% cotton plain weave fabric was used for this portion of the validation. The fabric samples were exposed to one pass of the nozzle at dial setting 8 with separation distance of 30.5 cm, were allowed to dry, sprayed with a potato starch solution to activate the fluorescein dye, and evaluated under black lights to determine deposition distribution of the dye particles.

A wide variety of nozzle types are commonly found on agricultural sprayers. The nozzle chosen for this study was of the hydraulic type, where a pesticide solution is pressure forced through an orifice and the liquid is sheared into droplets. Generally, there are five classes of hydraulic-operated nozzles found in agricultural sprayers: (a) side-entry hollow cone, (b) disk-type solid-cone, (c) core-insert hollow-cone, (d) fan-spray, and (e) flooding. Solid-cone, hollow-cone, and fan-spray nozzles were initially evaluated for use with this spray system. The solid and hollow-cone nozzles produce circular spray patterns. In this spray system the nozzle travels in a sweeping motion causing extensive spray overlap when the cone nozzles are used making them unacceptable. In addition, the circular pattern resulted in reproducibility problems within the chamber. The fan-spray nozzle was chosen for the chamber because of the uniformity in pesticide distribution that can be obtained across fabric specimens, when used in conjunction with the sweeping motion of the nozzle from one end of the chamber to the other. This nozzle produced a flat slot-like pattern that worked well with this system easily overlapping the intended fabric test specimen width of 15.2 cm but not overlapping between specimens. This TeeJet® nozzle (model number 730023), manufactured by Spraying Systems Company, Wheaton, Illinois, provided a 52° angle of discharge at .087 liters per minute when operated at 27.5 N/cm^2. The volume mean diameter (vmd) of water spray droplets was 150 micrometers (μm), under 27.5 N/cm^2 of driving pressure. The rate of nozzle movement was determined by timing how long it took to travel a predetermined distance. Rate determination was based on five replications. The speed of the nozzle in traveling the length of the chamber was adjustable (Table 1). Except at the lowest dial settings where movement occurred (4 and 5), these rates were consistent (indicated by the low standard deviation) while the nozzle traveled in one direction. However, there were inconsistencies when traveling in opposite directions under the same dial setting 9. In all cases, except at the dial setting, the left to right movement had a lower rate than the right to left movement. This inconsistency was due to drag effects as the hose was pulled by the nozzle unit as it moves from right to left. Consistency of results required choosing one or the other of the two directions during actual testing. For the remaining calibration and validation testing, the left to right nozzle movement was used, and only dial settings 6 and above were evaluated.

Table 1. RATE OF NOZZLE MOVEMENT AT EACH DIAL SETTING

Dial Setting	Direction of Nozzle Movement	Mean Rate* cm/sec	SD* cm/sec
0-3	L to R+	nm**	...
0-3	R to L++	nm	...
4	L to R	1.468	1.360
4	R to L	2.083	0.059
5	L to R	3.099	0.026
5	R to L	3.472	0.019
6	L to R	4.163	0.007
6	R to L	4.425	0.013
7	L to R	4.981	0.006
7	R to L	5.080	0.002
8	L to R	5.522	0.005
8	R to L	5.639	0.007
9	L to R	5.773	0.002
9	R to L	6.350	0.003
10	L to R	5.908	0.006
10	R to L	6.350	0.003

*Mean and standard deviation (SD) based on five replications.

**nm - no movement

+L to R - Left to Right

++R to L -Right to Left

Chamber Parameters: Driving Pressure = 27.5 N/cm^2 Distance between nozzle and sample = 30.48 cm

Consistency of the amount of liquid delivered to each sample was determined by weight. Validation of the consistency of the total coverage (volume/unit area), in each of the four slots was made following exposure to one pass of the spray nozzle. Water was the liquid used during this testing procedure. Precision was determined by replication. The collector plates were weighed before and after each spray exposure to determine the amount of liquid delivered at each location. Using this method (volume/unit area), a calibration was made between nozzle sweep speed and the amount of liquid delivered at three dial settings with separation distance between the nozzle and collector plate set at 30.5 cm. No dial setting below 6 was chosen for testing because of the high volume of liquid delivered due to the slow rate of nozzle movement and the increased standard deviation described earlier. Only dial settings of 6, 8, and 10 were evaluated to show significant differences in rates. Results showed reproducibility and consistency from position to position in passes made in the same direction (left to right) of the moving nozzle at the three dial settings (Table 2).

Table 2. SPRAY CHAMBER VALIDATION: LIQUID DELIVERY

	Amount of Liquid Delivered, gm/cm^2					
Dial		Slot				
Setting	A	B	C	D	Mean[*]	SD[+]
6	0.020	0.020	0.021	0.021	0.021	0.0006
8	0.015	0.016	0.016	0.016	0.016	0.0004
10	0.014	0.015	0.015	0.015	0.015	0.0004

[*] Mean based on three replications.

[+] Standard deviations between locations (slots) at three dial settings.

Chamber Parameters: Driving Pressure = 27.5 N/cm^2

Distance between nozzle and sample = 30.48 cm

Pressure was controlled using a regulator, and the possible variation in pressure was continuous. The effect of pressure on droplet size and spray pattern was evaluated. Droplet size was affected by the amount of hydraulic driving pressure used. Droplet size distribution was measured at pressures of 13.8 Newton/square centimeter (N/cm^2), 20.6 N/cm^2, 27.5 N/cm^2, 34.4 N/cm^2, and 41.3 N/cm^2. (These pressures correlate with commonly used English units of 20 pounds per square inch (psi), 30 psi, 40 psi, 50 psi, and 60 psi.) This range provided the maximum and minimum measurable range available. The droplet size was determined by covering a microscope slide with a thin layer of castor oil and exposing it to the spray (water) from TeeJet® nozzle 730023. The separation distance between nozzle and slide was constant at 30.5 cm. The nozzle remained stationary, and the slide was inserted for 1.5 seconds and then removed. The slide was immediately observed using a Projection 4002 (Heerburgs), and the droplets within a predetermined area were measured and counted to give a droplet-frequency distribution. Five replications at each pressure were evaluated. Results of the distribution are in Figure 3 and Table 3. According to Pratt et al. (6) the size of the droplets are classified as aerosols and fogs. As the driving pressure increases, the

Table 3. PRESSURE'S EFFECT ON DROPLET SIZE & DISTRIBUTION

Pressure, N/cm2	Droplet Size Range µmx10^3	TotalNumber of Droplets	Most Frequent Size, µmx10^3	Mean Size* µmx10^3	SD+ µmx10^3
13.8	0.1 - 1.5	59	1.0	0.861	0.882
20.6	0.1 - 1.5	152	0.8	0.753	1.045
27.5	0.1 - 1.5	201	0.5	0.475	0.276
34.4	0.1 - 0.8	142	0.1	0.232	0.176
41.3	0.1 - 0.6	144	0.1	0.232	0.233

*Mean size and +standard deviation (SD) based on five replications.

Chamber Parameters: Distance between nozzle and sample = 30.48 cm

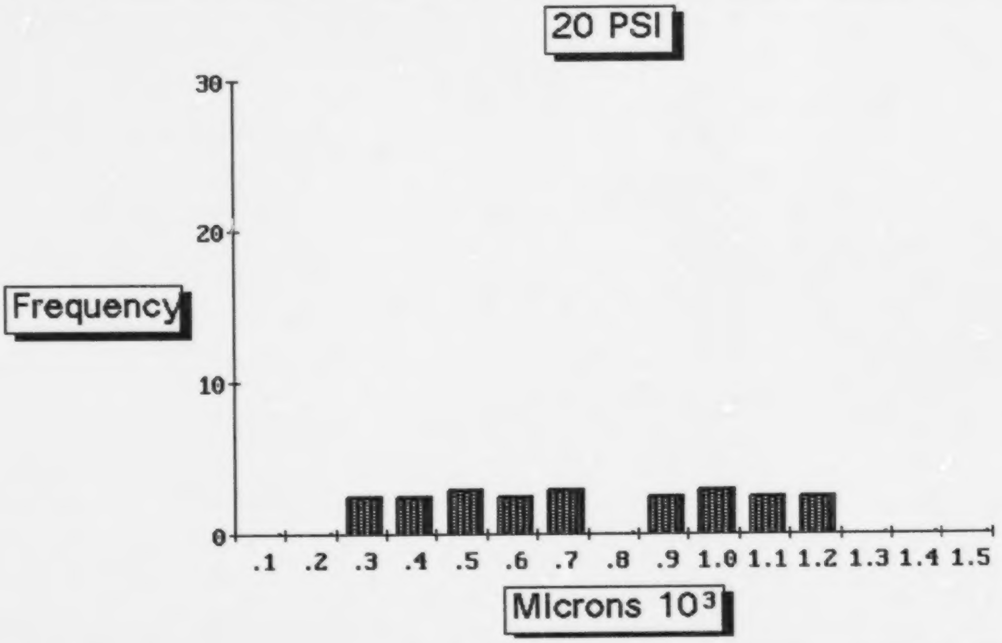


Figure 3. Droplet Distribution at Varying Pressures

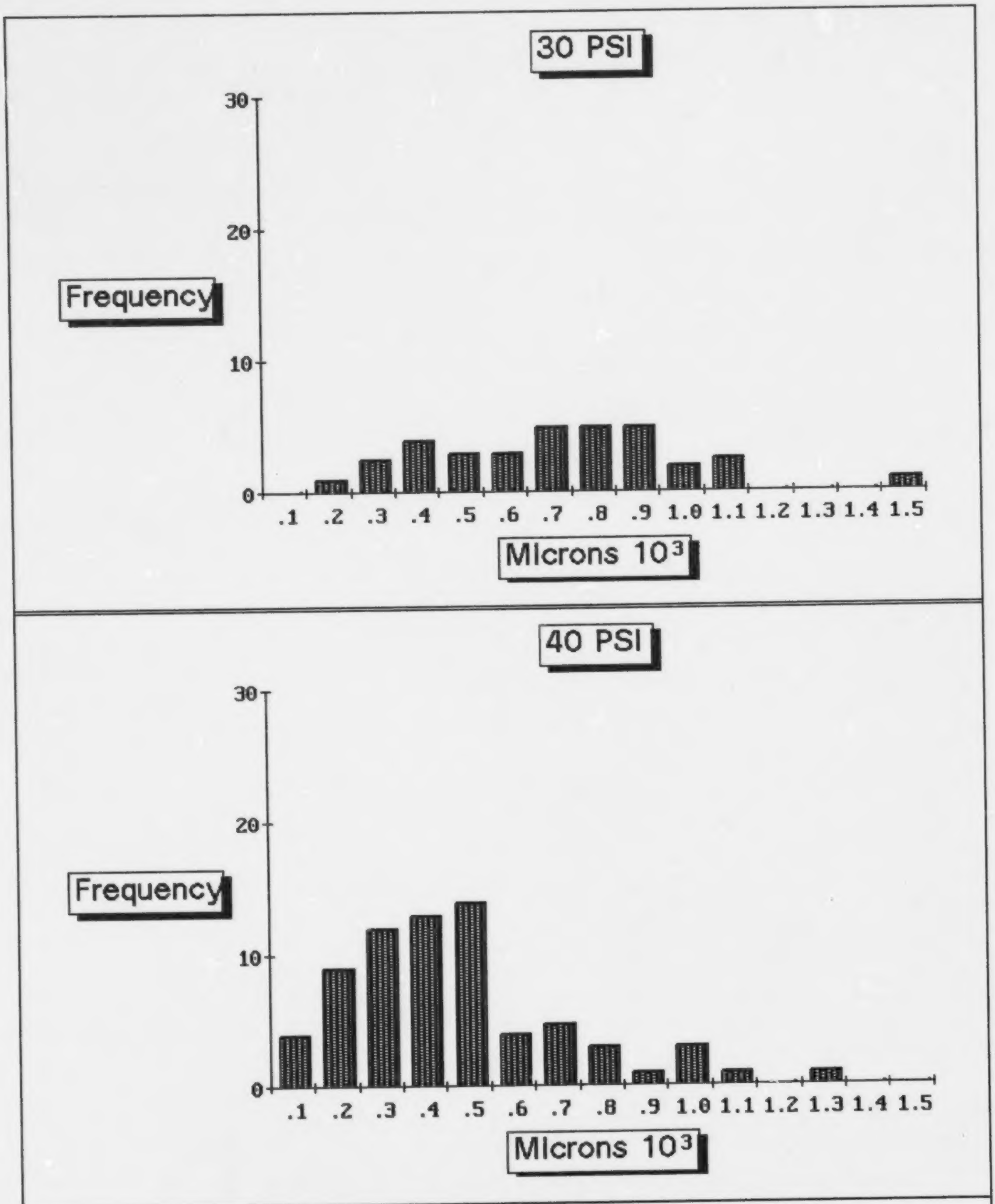


Figure 3. (continued)

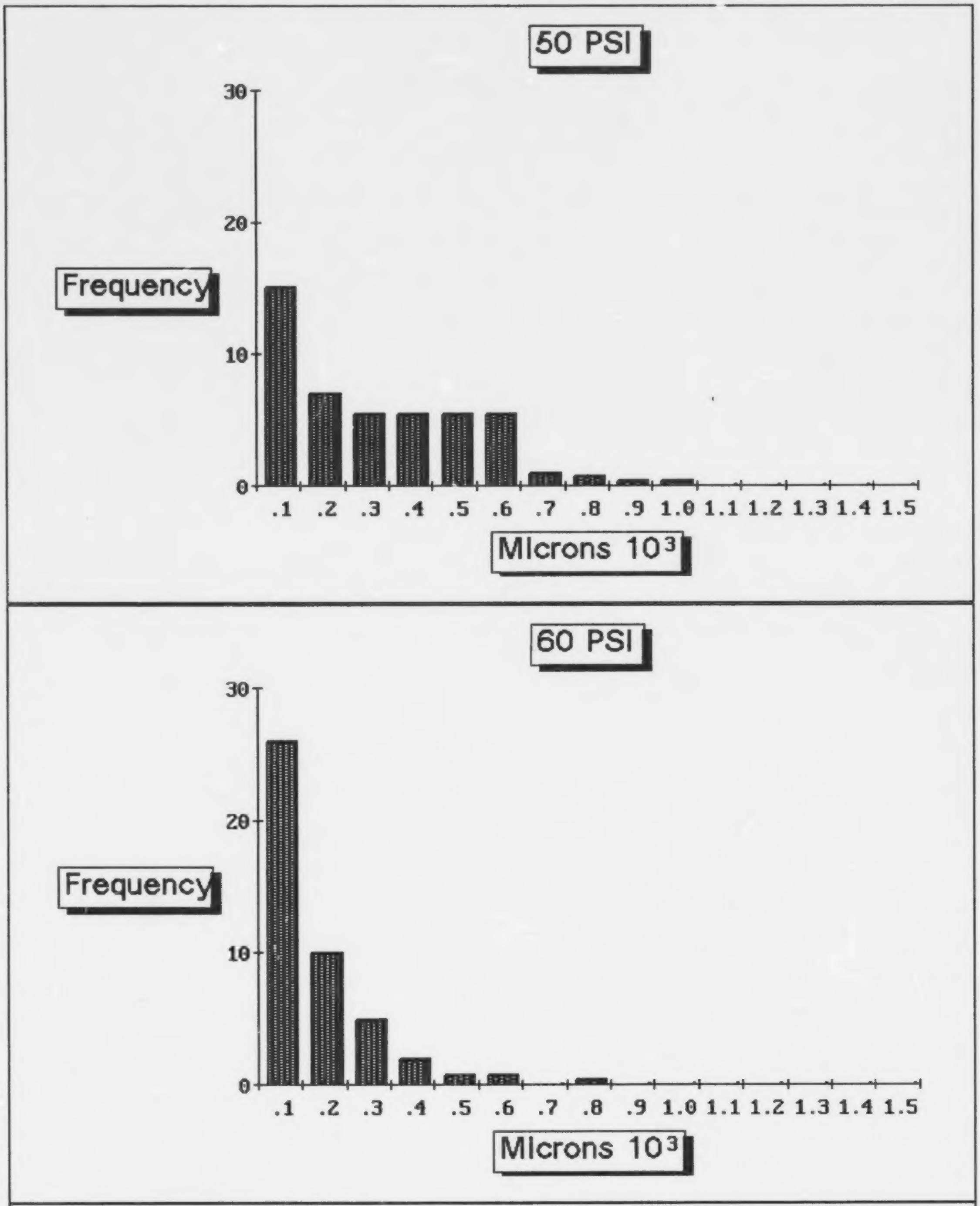


Figure 3. (continued)

size of the droplet decreases, and the droplet size range also decreases. However, the number of droplets collected on the slide peaked at pressure of 27.5 N/cm^2. As the pressure was increased after this point, the spray began to hang in the air and drift, producing a fog rather than aerosol. The result was a reduction in the number of droplets seen on the slide. Reproducibility also decreased as indicated by the standard deviation at 41.3 N/m^2.

Pressure also affects the spray pattern the fabrics are exposed to. Pressures of 13.8 N/cm^2, 27.5 N/cm^2, and 41.3 N/cm^2 were used to evaluate the fan-spray pattern. At 13.8 N/cm^2 a 15° angle fan was produced but did not provide complete coverage of the fabric sample area. The outer edge of the spray was more heavily concentrated than liquid delivery in the middle of the spray as indicated using fluorescein dye technique. A driving pressure of 27.5 N/cm^2 produced a 52° angle fan and good dispersion of spray pattern. This pattern covered the fabric sample area. When using 41.3 N/cm^2, an 87° angle fan was produced, and a drifting of spray within the chamber was present. Such factors contributed to poor reproducibility.

The spray system was designed so that the distance between the nozzle tip and test specimen location could be adjusted. Three distances were chosen to evaluate spray nozzle-fabric separation and liquid delivery. Data was completed using the previously described technique of the use of collector plates to quantify coverage (volume/unit area). Results in Table 4 show how liquid coverage is affected by the separation of test sample location and nozzle tip. Liquid coverage can be changed by approximately 60 percent simply by adjusting the height of the spray head in the system from the lowest to highest positions.

Table 4. EFFECT OF SEPARATION BETWEEN FABRIC AND NOZZLE

Distance, cm	Liquid Amount, Mean g/cm^2	SD* g/cm^2
25.40	0.012	.00040
30.48	0.016	.00045
38.10	0.019	.00007

*Mean size and standard deviation (SD) based on three replications.

Chamber Parameters: Dial setting = 8 Driving pressure = 27.5 N/cm^2

Conclusion

The laboratory spray system delivered a controlled amount of liquid to fabric samples. Tests of the equipment indicated that it could be adjusted so that the spray pattern was uniform and the amount of liquid delivered to each sample was consistent. This chamber can be used under a fume hood to minimize laboratory research exposure.

This chamber allowed for reproducible laboratory testing of fabric samples exposed to aerosol droplets similar to what has been reported in field situations. The cost was reduced by moving testing from the field to the laboratory, while the hazards were lessened through the closed system design and the utilization of a chemical exhaust hood. This system provided a method for laboratory screening of fabrics for pesticide penetration. The data collected will aid in the understanding of fabric and pesticide variables in the penetration process. Verification can then be made through field studies on fabrics which perform well in the less costly laboratory testing. These combined efforts will increase the dependability and speed of results leading to fabric recommendations for protective apparel for pesticide application.

SECTION 5

PESTICIDE PENETRATION THROUGH FABRICS

EFFECT OF FABRIC CHARACTERISTICS ON PESTICIDE PENETRATION

The use of protective apparel as a barrier from dermal exposure to pesticide residues is considered vital in providing some measure of protection. To date, research on apparel as a protective barrier has identified some fabrics which allow minimal or no penetration of pesticide particulates. The fabric itself is the barrier. Previous research has also shown that fiber content and fabric finish may influence the penetration of pesticides through fabrics (7,8,9). And one study (2) has shown that fabric geometry may affect the droplet spread influencing absorption characteristics. To date, the research in this area has been conducted on isolated fabrics with little consideration given to other variables in the fabrics which may affect penetration. Since fabric characteristics vary greatly, the effect of these characteristics on pesticide penetration should be investigated.

An exploratory investigation was designed to determine the effect of various fabric characteristics and their contribution to the fabric's performance as a barrier against pesticide penetration. Twelve different fabrics were evaluated and eight characteristics were measured for each fabric. Four pesticides representing two chemical classes were used.

Fabrics

The fabrics were chosen to represent those readily available to agricultural workers, plus two experimental fabrics. Three of the fabrics--denim, chambray, and work-weight twill--are commonly found in ready-to-wear apparel and are easily accessible to the agricultural worker. Based on previous studies (9) showing an increase in protection against penetration when water repellent finishes are applied, a commercial water-repellent finish was applied to these fabrics. Formulation for this finish was 7% Zepel D, 10% Norane F, and 0.4% Mykon NRW-3 and 82.6% water. Processing was carried out with two dips and two nips (textile finishing measurements) under 20 psi pressure and then cured for 3 min at 110°C. This resulted in a wet pickup of approximately 90% for denim and chambray and approximately 46% for the work-weight twill fabric. Denim, chambray, and work-weight twill were evaluated with and without the water-repellent finish.

Four of the fabrics examined are currently available in specially designed protective clothing for the application of pesticides. These include Tyvek®, polyethylene-coated Tyvek®, Saranex-coated Tyvek®, and Gore Tex®, 50/50 cotton/polyester woven fabric and a 100% polyester jersey-knit back. The woven fabric was evaluated as the face fabric. Two of the fabrics were nonwoven experimental fabrics treated with repellent finishes that could be used for protective clothing. Complete fabric descriptions are listed in Table 5.

Fabric characteristics that have shown some influence on penetration in previous studies (2,4), or theoretically could influence transmission, were chosen for this study. These characteristics are

Table 5. FABRIC DESCRIPTIONS: INITIAL STUDY

Code	Common name	Fiber Content	Construction	Finish
W25	Denim	100% cotton	Woven--twill	None
W26	Denim--Fl	100% cotton	Woven--twill	Fl
W23	Chambray	100% cotton	Woven--plain	None
W24	Chambray--Fl	100% cotton	Woven-plain	Fl
W21	Twill	65/35 cot/poly	Woven--twill	None
W22	Twill--Fl	65/35 cot/poly	Woven--twill	Fl
N1	Tyvek®	100% olefin	Nonwoven--PB	None
N2a	Tyvek® --PE	100% olefin	Nonwoven--PB	PE
N2b	Tyvek® --Saranex	100% olefin	Nonwoven--PB	Saranex
N13	Gore Tex®	65/35 cot/poly	Comp--W/NW/K	None
Ex 1	Experiment a-1	Polypropylene	Comp--SB/MB/SB	Repellent*
Ex 2	Experiment a-2	Polyester	Nonwoven--PB/SB	Repellent*

MB--Melt blown
SB--Spun bonded
PB--Point bonded
*Formulation unknown due to fabric manufacturer trademarks

Fl--Fluorocarbon water repellent
Poly--Polyester
Comp--Composite

PE-Polyethylene
NW-Nonwoven
COT-Cotton
W-Woven K-Knit

Table 6. FABRIC CHARACTERISTICS: INITIAL STUDY

Fabric	Thickness (mm)	Weight (gm/m^2)	Air Permeability ($m^3/sec/m^2$)	Spray Rating	Yarn warp	Count fill	Surface Energy (dynes/cm)	Surface Energy Rating
Denim	0.66	274.0	.02	0	52	44	35.00	(1)
Denim--FL	0.66	287.6	.02	50	52	44	30.62	(2)
Chambray	0.30	116.9	.07	0	58	52	35.00	(1)
Chambray--FL	0.30	123.5	.49	70	58	52	28.63	(5)
Twill	0.43	235.0	.07	50	50	58	35.00	(1)
Twill--Fl	0.36	233.6	.09	50	50	57	28.63	(5)
Tyvek®	0.10	36.4	.0	60	NA	NA	30.16	(3)
Tyvek®-PE	0.15	56.0	.0	100	NA	NA	22.30	(8)
Tyvek®-Sar	0.18	98.9	.0	100	NA	NA	22.30	(8)
Gore-Tex®	0.38	165.4	.0	0	60	57	35.00	(1)
Ex 1	1.52	64.8	.05	100	NA	NA	22.30	(8)
Ex 2	0.18	42.8	1.29	100	NA	NA	22.30	(8)

The following methods were used:
Thickness - ASTM D177-64
Surface Energy Rating - AATCC 118-1983
Yarn Count - ASTM D3775-79

Spray Rating - AATCC 22-1980
Weight - ASTM D3776-79
NA-Not Applicable

fiber content, fabric construction, surface fabric construction, surface treatment, yarn count, weight, thickness, air permeability, spray rating, and surface tension. The test methods used and results for each fabric are listed in Table 6.

Exposure

The fabric sample exposed to pesticide spray was a four-layer composite, 15.2 cm x 15.2 cm square consisting of the test fabric, a collector layer, foil, and foil backing (Figure 4). In this study, the test fabric is being evaluated for its ability to prevent pesticide penetration by analyzing the quantity of pesticides found on the collector layer. The collector layer was a 50% cotton/50% polyester blend tee-shirt fabric supplied by Standard Knitting Mills of Knoxville, Tennessee. The four layers were combined according to standard procedures (see Appendix A). A random order of exposure was determined statistically (see Appendix C), using an incomplete block design to minimize any systematic errors in the spray system.

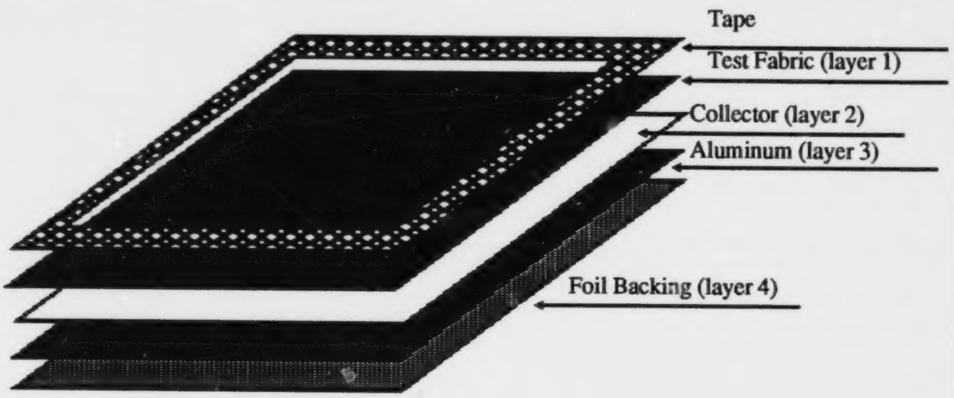


Figure 4. Illustration of MultiLayer Sample

Pesticide solutions were prepared to produce a 0.12% concentration. The spray chamber developed in this project was used to expose the fabric specimen. The pesticide was applied using a TeeJet® fan-spray nozzle no. 730023 obtained from Spray Systems Company. The nozzle height remains constant at 30.48 cm above the fabric specimen surface. One pass of the nozzle, producing a 2.65 sec duration from sample edge to sample edge and delivering 3.5 grams of liquid, was made (see Appendix A).

After exposure, the fabrics were allowed to dry for one hour. A 7.62 cm x 2.54 cm strip specimen was removed from the center of the fabric and pesticide extracted (see Appendix A). Using gas chromatography analysis techniques, the extract was analyzed and the amount of pesticide that penetrated the top layer of fabric, as found on the collector layer, was determined. A Varian 3600 gas chromatograph was used with an electron capture detector for the chlorinated hydrocarbon pesticides (Captan and Dicofol) and a nitrogen-phosphorous thermionic specific detector to analyze the organophosphate pesticides (see Appendix B). Extraction efficiencies were performed on all four pesticides prior to testing (see Appendix A).

Results and Discussion

An Analysis of Variance (ANOVA) determined that the fabrics did provide varying degrees of protection against pesticide penetration (Table 7) (see Appendix C). The amount of pesticide obtained on the collector layer is listed in Table 8. Using Duncan's multiple range test, the fabrics were grouped as to the amount of pesticide that penetrated to the collection layer (Table 9). Those fabrics in Group A allowed the largest amount of pesticide to penetrate, providing the poorest protection. Fabrics in Group D allowed no detectable penetration of pesticide, providing excellent protection. Fabrics in Groups B and C are classified as having below average and above average protection, respectively.

The chambray fabrics-both treated and untreated in Groups A and B for all pesticides provided poor or below average protection against pesticide penetration. These fabrics had the lowest thickness of the woven fabrics tested and were of plain weave construction. Fabrics in Group D were the coated Tyvek® fabrics, both having impermeable coatings. Untreated denim and twill fabrics were also in this group for three of the four pesticides (Table 9). They were the two thickest fabrics tested and both are of twill construction, indicating these characteristics may play an

Table 7. ANALYSIS OF VARIANCE: INITIAL STUDY

Pesticide	Source	df	Sum of Squares	MS	F Value
Captan	Fabric	9	85.59	9.29	11.91*
	Model	43	33.52	0.78	
	Total	52	117.11		
Dicofol	Fabric	2	2.41	1.21	16.64*
	Model	11	0.80	3.21	
	Total	13	3.21		
Ethion	Fabric	2	3.95	1.97	31.40*
	Model	11	0.69	0.06	
	Total	13	4.64		
Methyl Parathion	Fabric	4	4.32	1.08	2.43
	Model	18	8.30	0.46	
	Total	22	12.62		

*Significant at the 0.05 level

Table 8. PESTICIDE PENETRATION: INITIAL STUDY

Pesticide Amount Penetrated ($\mu g/cm^2$)

Code/Fabric	Captan	SD	Dicofol	SD	Ethion	SD	Methyl Parathion	SD
W25/Denim	(5).014	.004	(5)ND[+]	.000	(5)ND	.000	(5)ND	.000
W26/Denim-F1	(4).021	.007	(5)ND	.000	(5)ND	.000	(5)ND	.000
W23/Chambray	(5).450	.116	(5)0.234	.035	(4).040	.006	(4).047	.009
W24/Chambray-Fl	(4).064	.009	(5)0.162	.012	(5).068	.002	(4).033	.008
W21/Twill	(5).007	.002	(5)ND	.000	(5)ND	.000	(5)ND	.000
W22/Twill-Fl	(3).021	.010	(5)ND	.000	(5)ND	.000	(5)ND	.000
N1 /Tyvek®	(5).246	.021	(5)ND	.000	(5)ND	.000	(5)018	.005
N2a/Tyvek®-PE	(5)ND	.000	(5)ND	.000	(5)ND	.000	(5)ND	.000
N2bTyvek®-Sar	(5)ND	.000	(5)ND	.000	(5)ND	.000	(5)ND	.000
N13/Gore Tex®	(4).060	.020	(5)ND	.000	(5)ND	.000	(5)ND	.000
Ex. 1	(4).007	.017	(5)ND	.000	(5)ND	.000	(5).017	.040
Ex. 2	(4).078	.021	(4).084	.017	(5).012	.006	(5).055	.020

+ND non detectable (#) -number of fabric replications SD - Standard Deviation

Table 9. DUNCAN'S MULTIPLE RANGE TEST: INITIAL STUDY

Pesticide	Variable	Pesticide Amount Penetrated ($\mu g/cm^2$)	Groupings
Captan	Chambray	0.450	A
	Tyvek®	0.246	B
	Ex. 2	0.078	B
	Chambray-Fl	0.064	B
	Gore Tex®	0.060	B-C
	Twill-Fl	0.021	B-C
	Denim-Fl	0.021	C
	Denim	0.014	C
	Ex. 1	0.007	C
	Twill	0.007	C
	Tyvek®-PE	ND	D
	Tyvek®-Sar	ND	D
Dicofol	Chambray	0.234	A
	Chambray-Fl	0.162	B
	Ex. 2	0.084	C
	Denim	ND	D
	Denim-Fl	ND	D
	Twill	ND	D
	Twill-Fl	ND	D
	Tyvek®	ND	D
	Tyvek®-PE	ND	D
	Tyvek®-Sar	ND	D
	Gore Tex®	ND	D
	Ex. 1	ND	D
Ethion	Chambray-Fl	0.068	A
	Chambray	0.040	B
	Ex. 2	0.012	C
	Denim	ND	D
	Denim-Fl	ND	D
	Twill	ND	D
	Twill-Fl	ND	D
	Tyvek®	ND	D
	Tyvek®-PE	ND	D
	Tyvek®-Sar	ND	D
	Gore Tex®	ND	D
	Ex. 1	ND	D
Methyl Parathion	Ex. 2	0.055	A
	Chambray	0.047	A-B
	Chambray-Fl	0.033	B-C
	Tyvek®	0.018	C-D
	Ex. 1	0.017	D
	Denim	ND	D
	Denim-Fl	ND	D
	Twill	ND	D
	Twill-Fl	ND	D
	Tyvek®-PE	ND	D
	Tyvek®-Sar	ND	D
	Gore Tex®	ND	D

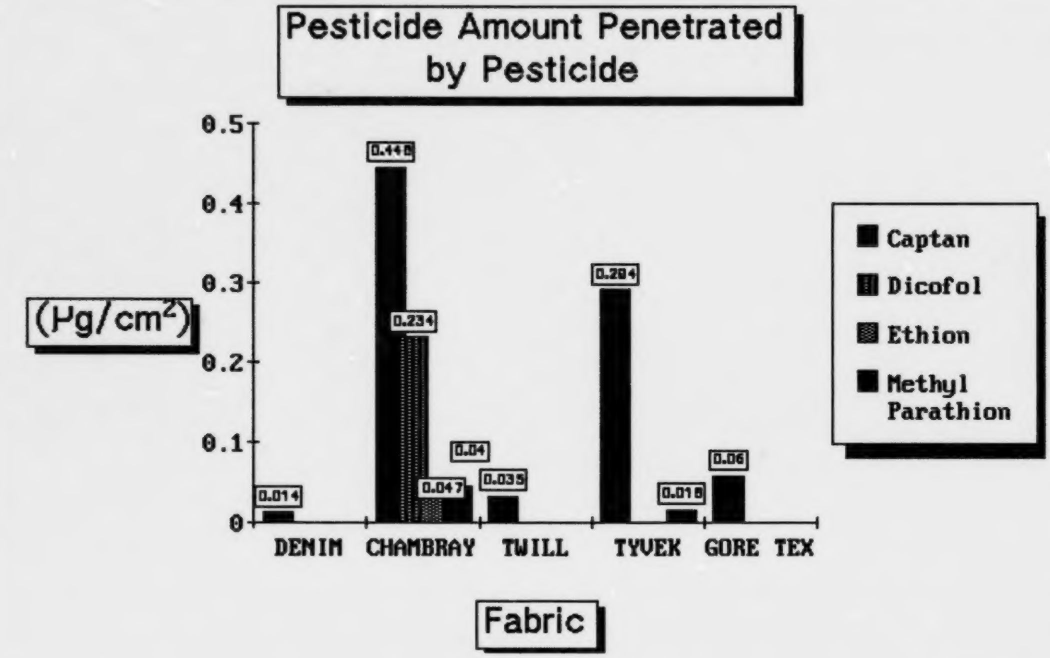


Figure 5. Pesticide Amount Penetrated by Pesticide

important role in preventing pesticide penetration through fabrics. A graphic representation (Figure 5) illustrates the pattern of penetration for the fabrics evaluated in this study. This figure, combining the data for treated and untreated fabrics, shows the major differences between base fabrics regardless of treatment.

Effect of Fabric Characteristics--

Spray Rating--Spray rating is the measurement of a fabric's water repellency and is determined by pouring a specific quantity of water through a funnel at a set distance above the fabric's surface, and is then evaluated by rating the wetting that occurs. A rating of 100 indicates there was no wetting of the fabric, and a rating of 0 indicates the fabric was readily wetted. Spray rating, however, did not consistently predict the ability of a fabric to prevent pesticide penetration (Figure 6). In this study, fabrics with a high spray rating provided excellent protection against pesticide penetration in all cases. However, denim fabrics with a repellency rating of 0 also provided excellent protection from three of the four pesticides, in contrast, unfinished chambray fabrics with a spray rating of 0 provided below average protection for three of the pesticides and was in the lowest group for the remaining pesticide.

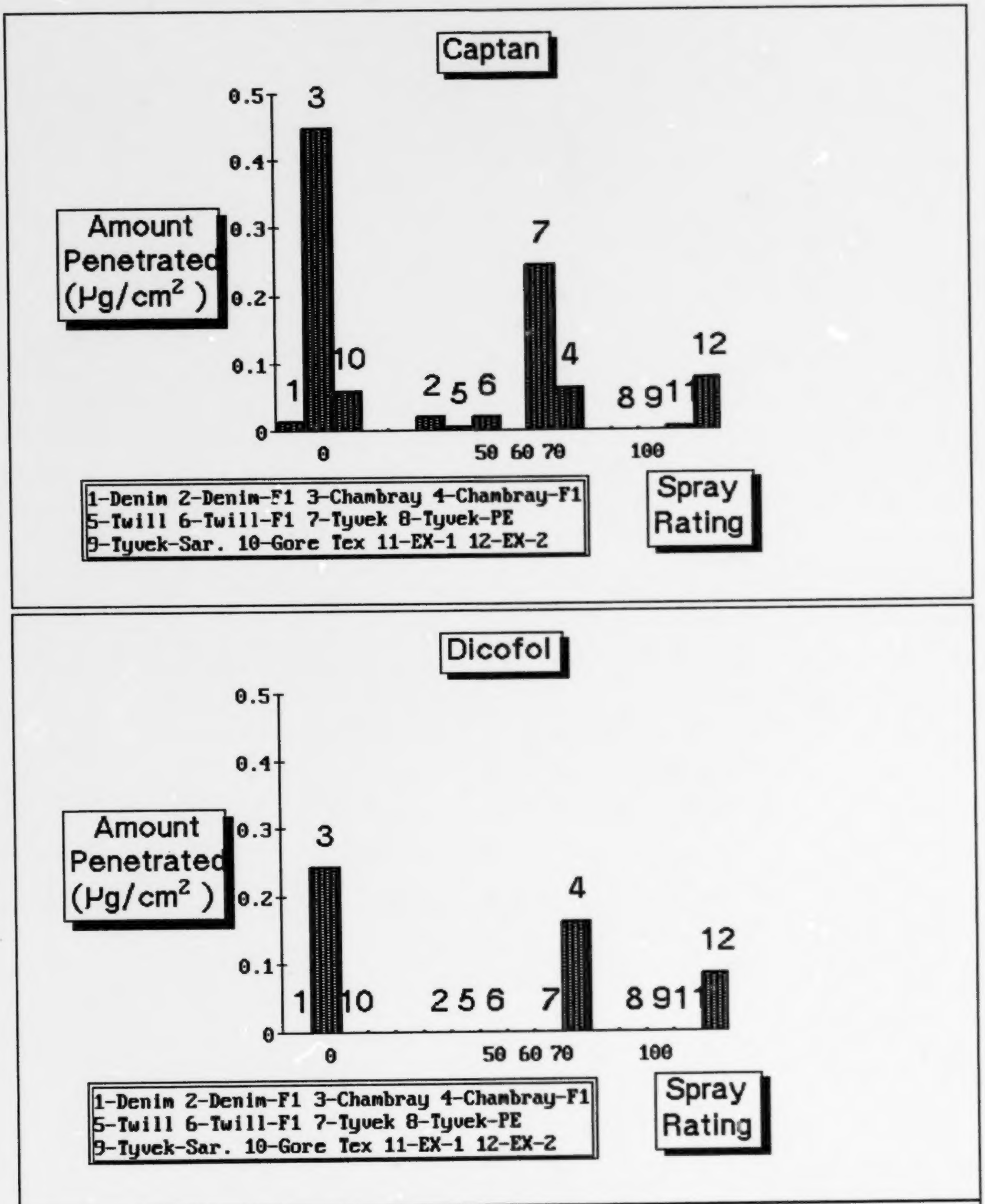


Figure 6. Spray Rating vs. Penetration by Pesticide

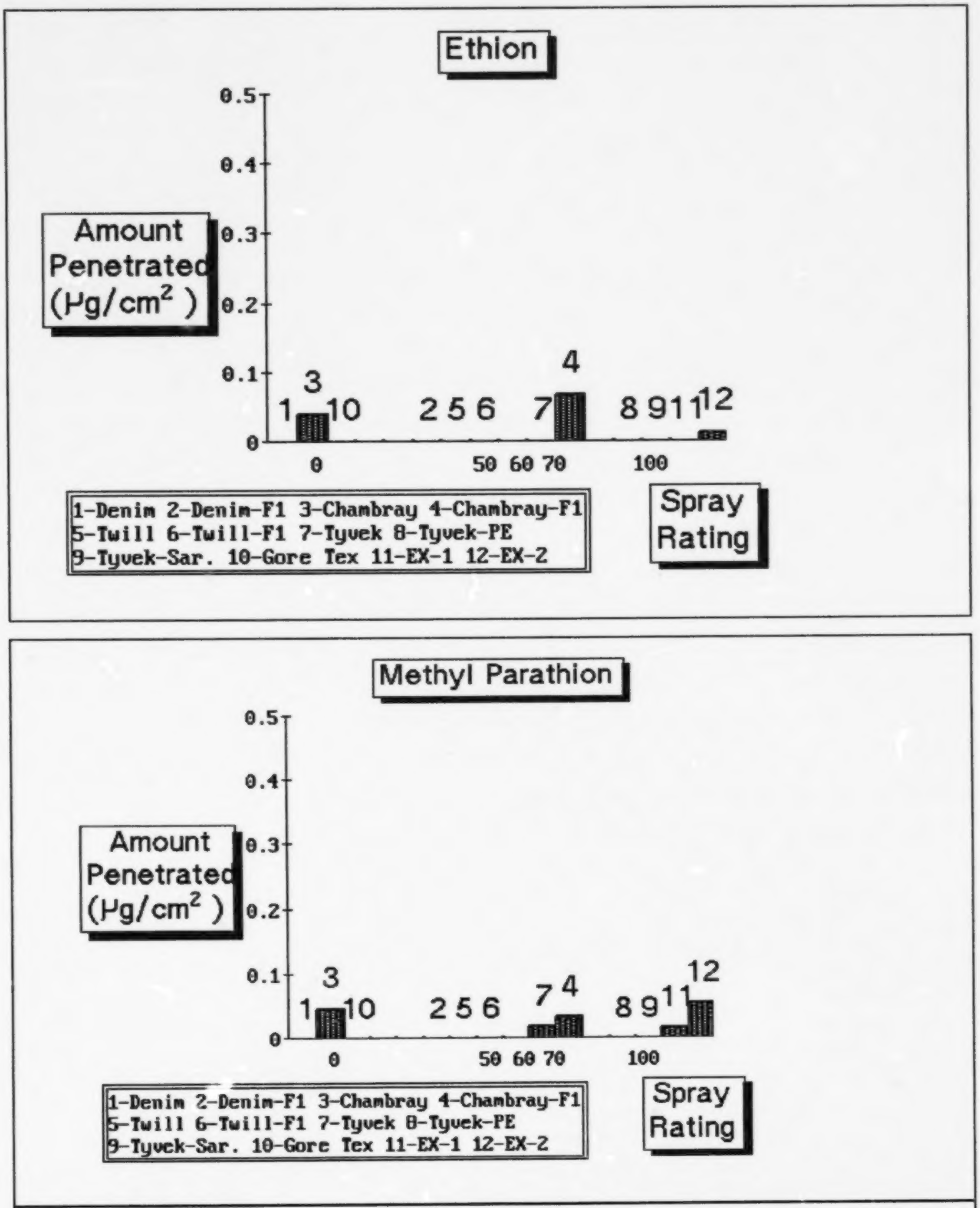


Figure 6. (continued)

Factors which may help explain why the spray rating does not correlate with pesticide penetration include differences in fabric thickness and fabric construction. Thickness and construction have been shown to influence the penetration of pesticides, and their influences were thought to be more powerful than that of the spray rating. It is theorized that spray rating may not relate directly to pesticide penetration due to other more influential characteristics, such as fiber content, fabric construction, and/or fabric weight and thickness. For example, denim (Fl), which had the lowest repellency rating, provided above average protection for one pesticide and excellent protection for the other three. Thus a discrepancy exists between spray rating indication and actual protection.

In addition, the testing procedures for determining repellency and penetration differ. The repellency test rating is completed immediately after the application of the liquid. The amount of pesticide penetration, however, is measured after applying the solution and allowing it to remain on the fabric for a minimum of one hour. Since penetration can be a function of time, this difference in time may affect the two measurements. Also, as time passed, the nature of the pesticide solution may be altered due to environmental conditions, decreasing the surface tension of the liquid allowing for increased spreading of the droplet and subsequent absorption.

Surface Energy--Surface energy categories were determined by using a series of solutions of known surface energy. The solution that wets the fabric surface is the rating assigned to the fabric. Using surface energy, it was not possible to predict the amount of pesticide penetration that occurred (Figure 7). When surface energy decreased, penetration did not always decrease. These results could be attributed to the test method. The surface energy determination is made after 30 seconds, compared with penetration being measured after one hour.

Surface Treatments--Of the 12 fabrics evaluated, seven had some type of finish, treatment, or coating applied. Three of these (denim, Chambray, and twill) were treated with a repellent fluorocarbon finish. Saranex® and polyethylene coatings were applied to the 100% spunbonded olefin (Tyvek®). The remaining two finishes were applied to nonwoven fabrics (Ex. 1 and Ex. 2) to increase repellency. These two experimental finishes were applied by the fabric manufacturers; therefore, their formulations are not available for disclosure in this study.

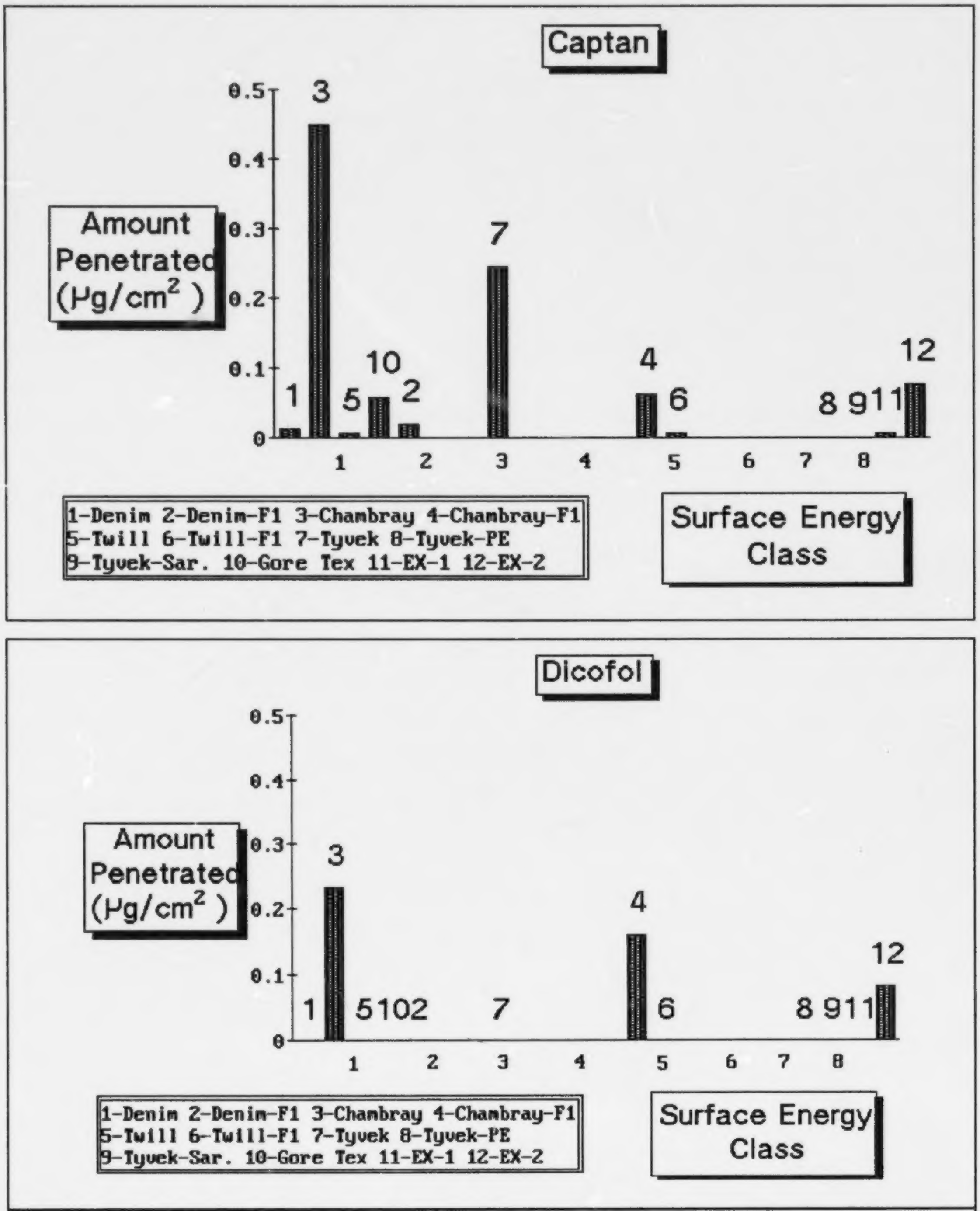


Figure 7. Surface Energy vs. Penetration by Pesticide

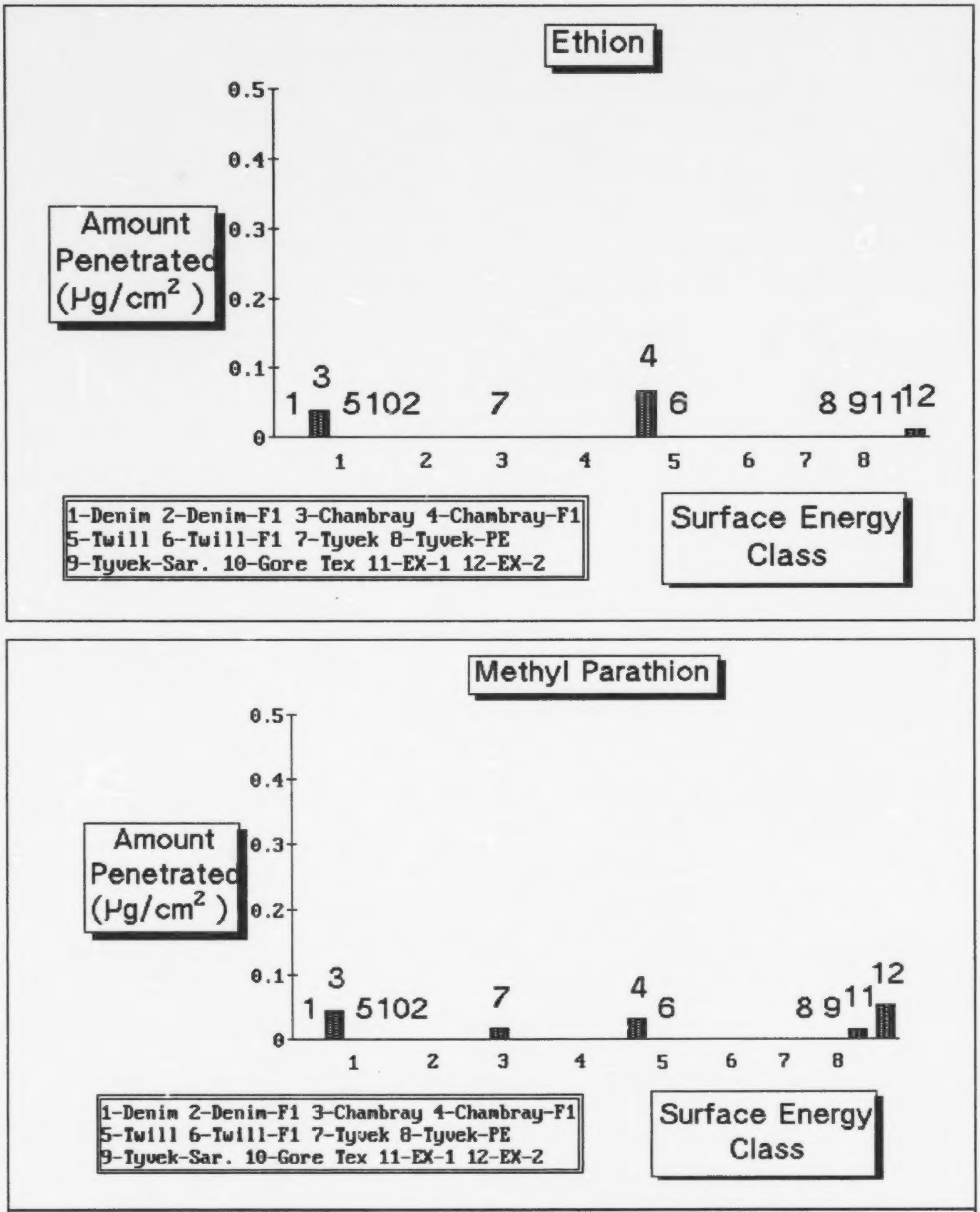


Figure 7. (continued)

The fabrics treated with the fluorocarbon finish showed improvement in protection for only the lightest weight-woven fabric, chambray, for two pesticides: Captan and Dicofol(Figure 8). With Ethion untreated fabric provided better protection than the treated fabric. The treated and untreated denim and twill provided protection from Methyl Parathion, Dicofol, and Ethion. For the pesticide Captan, the untreated fabric provided better protection than the treated fabric.

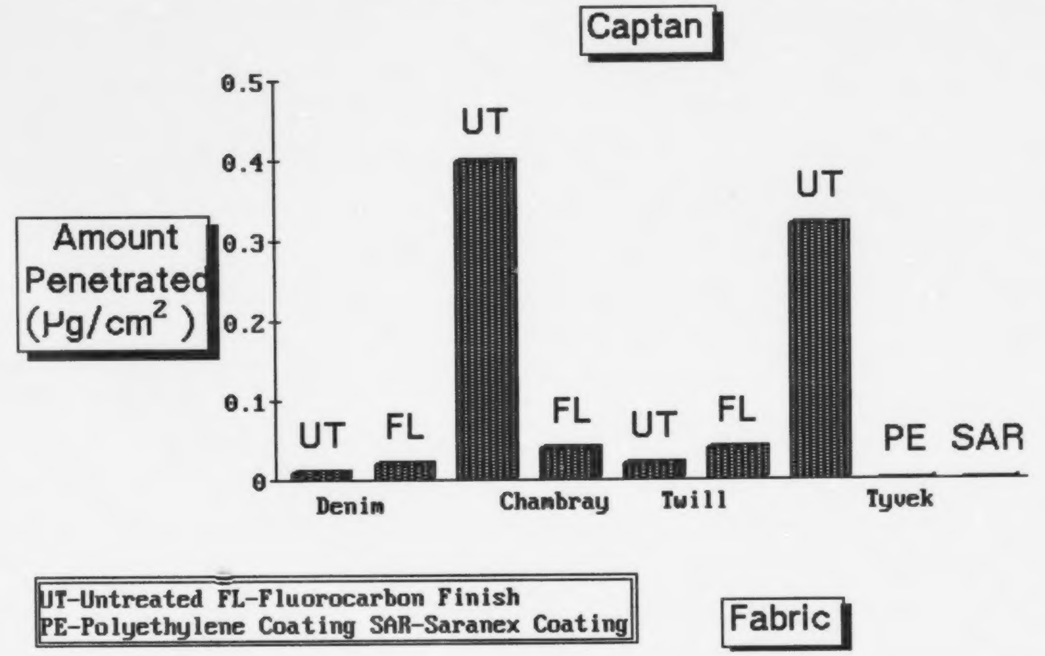
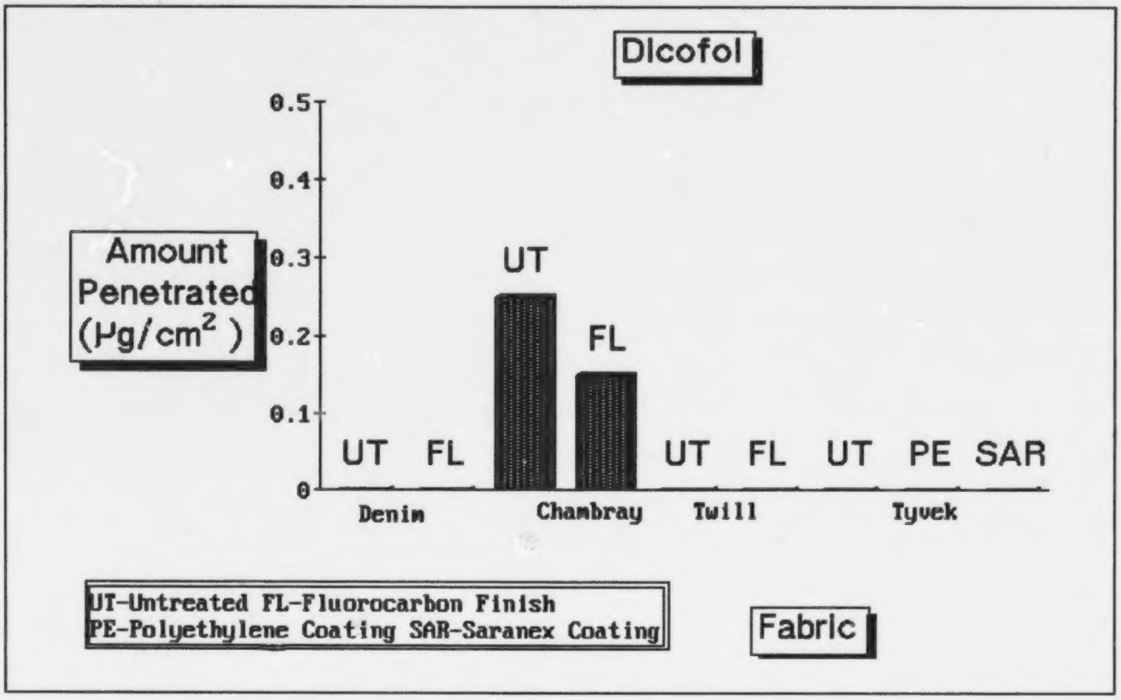


Figure 8. Comparisons of Treated and Untreated Fabrics



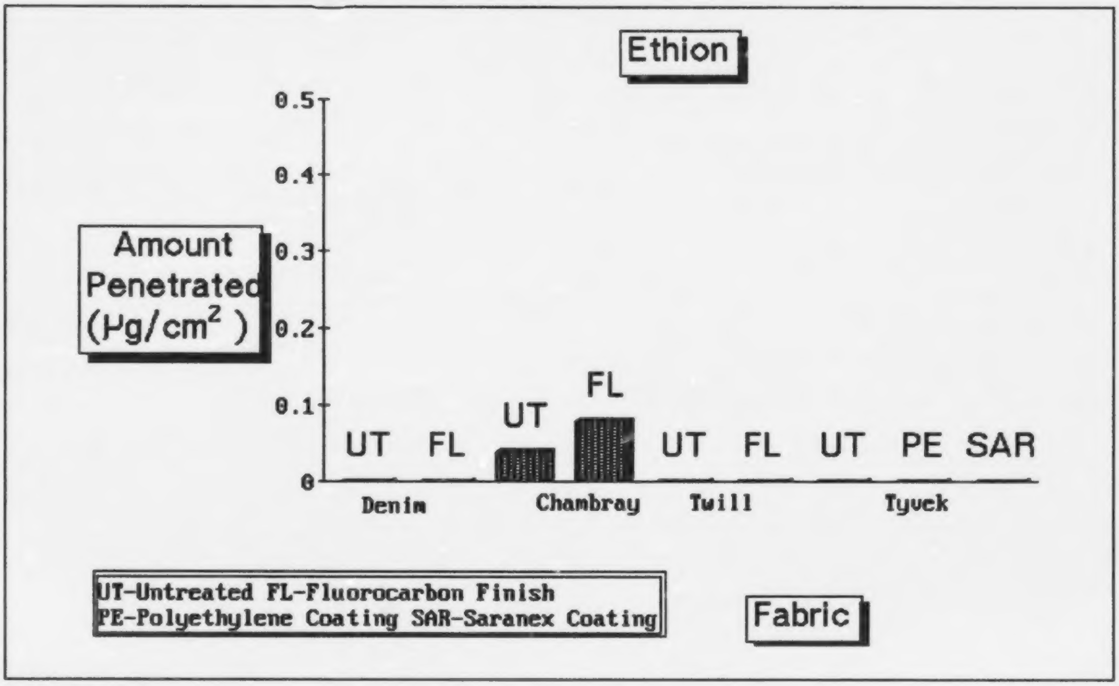


Figure 8. (continued)

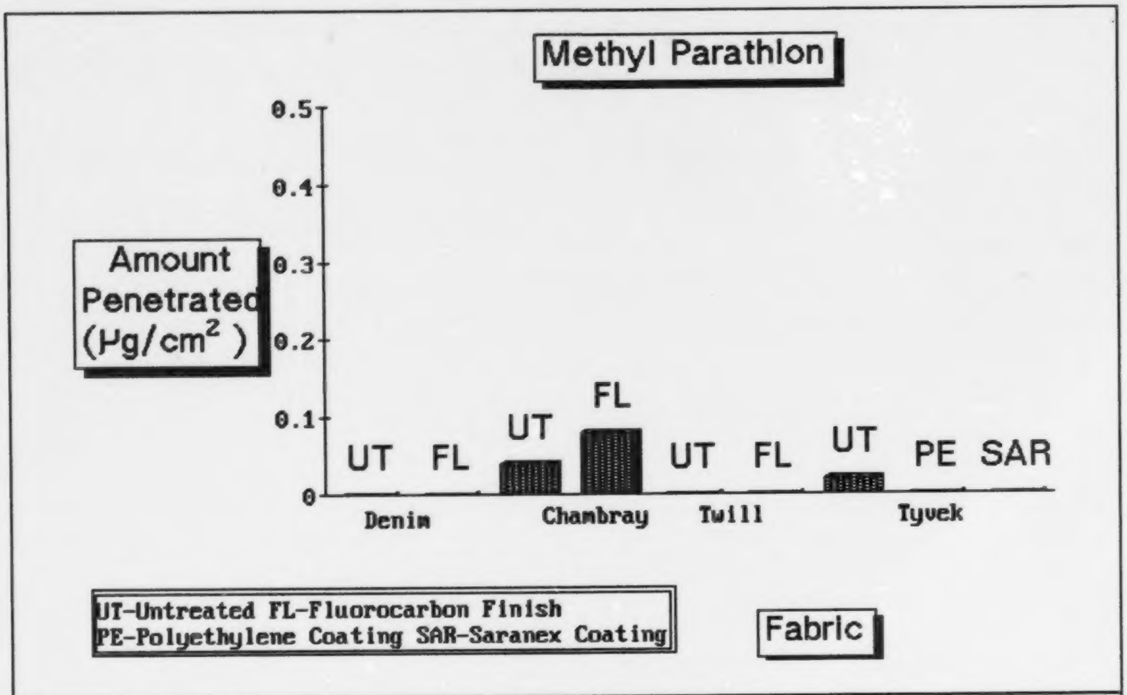


Figure 8. (continued)

The coated Tyvek® fabrics provided protection for all four pesticides. However, it is important to realize that these coatings are impermeable and may not meet the thermal demands of the pesticide applicator.

The nonwoven fabrics, Gore Tex® and Ex. 1 provided protection for the pesticides Dicofol and Ethion. They ranked between poor and average for Captan and Methyl Parathion. There were no untreated samples available for testing, so it is not possible to determine if treatment improved the ability of the fabric to prevent pesticide penetration.

The results indicate not all surface treatments reduce pesticide penetration. The treatments classified as coatings did eliminate penetration of the pesticide. However, the application of fluorocarbon treatments did not always enhance protection.

Air Permeability--Air permeability was measured using a Gurley Permeometer, model TY1253. Air permeability is the measure of the rate at which air travels through a fabric at a specified pressure drop. This is related to the porosity of the fabric. In theory, particle penetration may also be related to porosity of the fabric: the more porous the fabric, the more opportunity for penetration to occur. However, in this study the amount of pesticide penetration was not directly related to the air permeability measurement of the fabric. (Figure 9 and Table 6). Two of the fabrics that exhibited zero air permeability (Saranex and polyethylene-coated Tyvek®) allowed no penetration for any of the four pesticides to occur. Both of these fabrics were coated with a nonpermeable finish, so zero air permeability was expected. A third fabric (Gore Tex®) had zero air permeability and provided

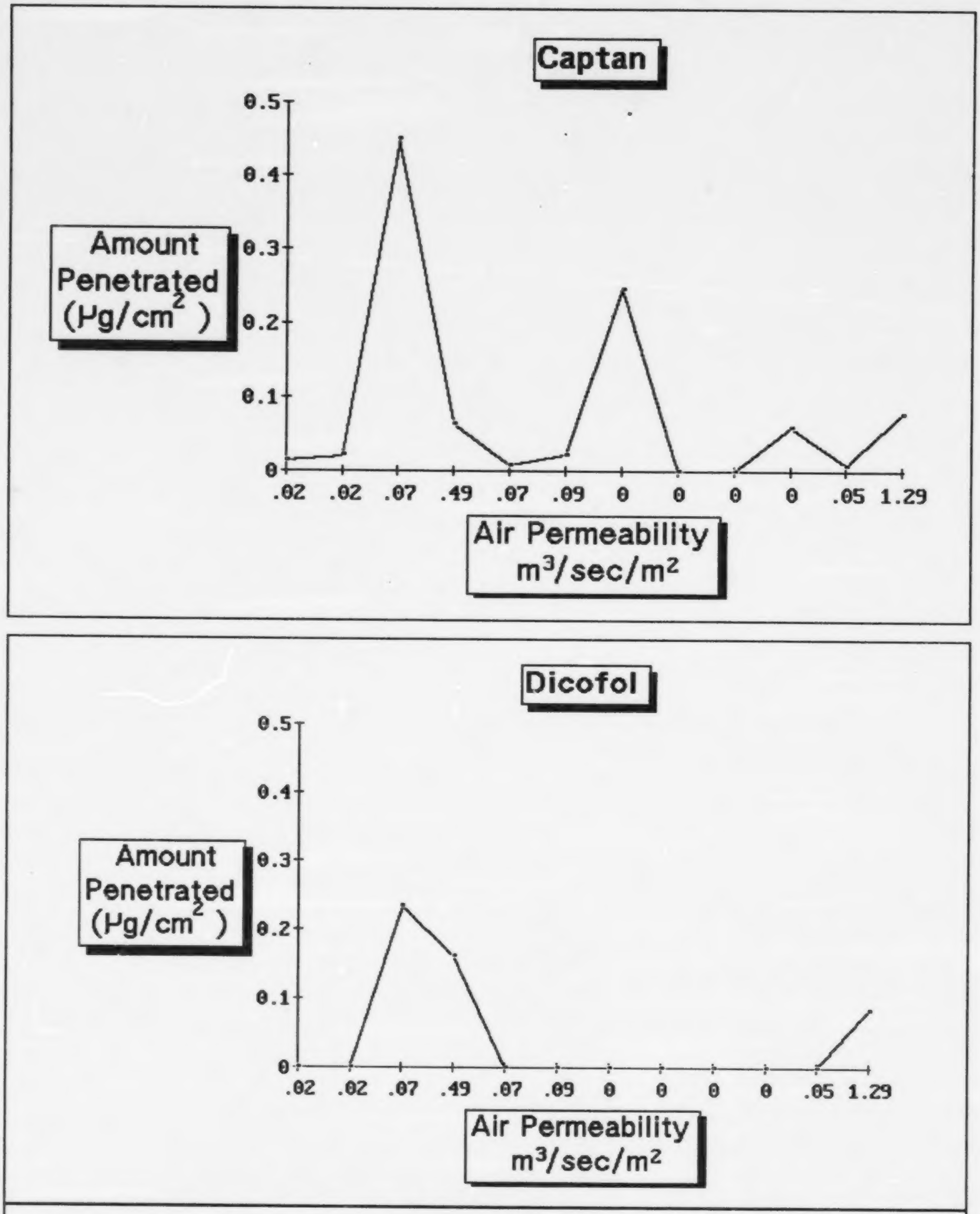
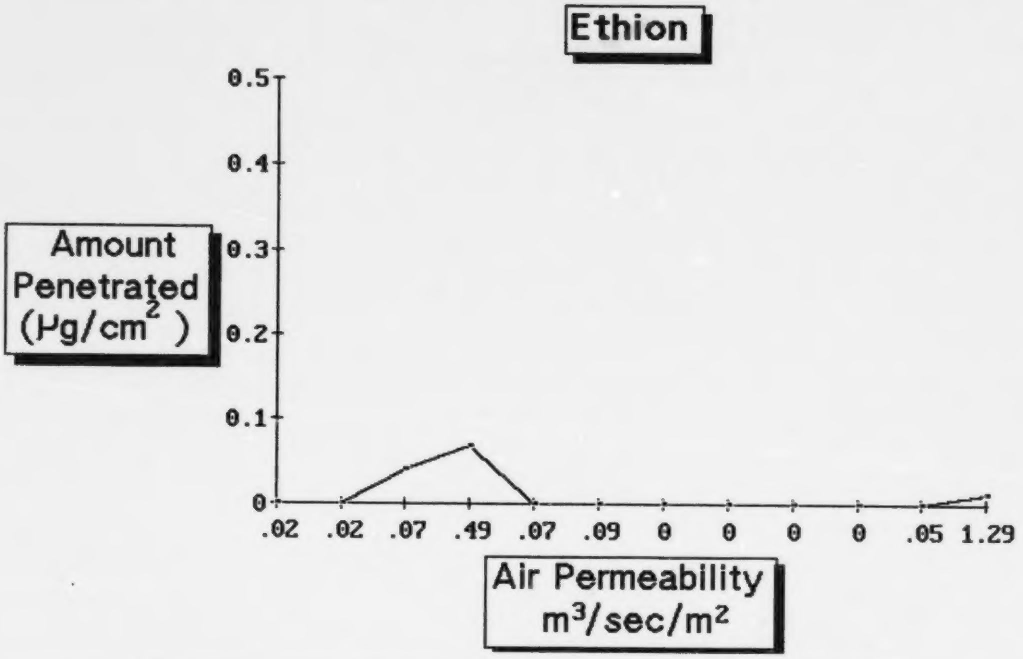


Figure 9. Air Permeability vs. Penetration by Pesticide



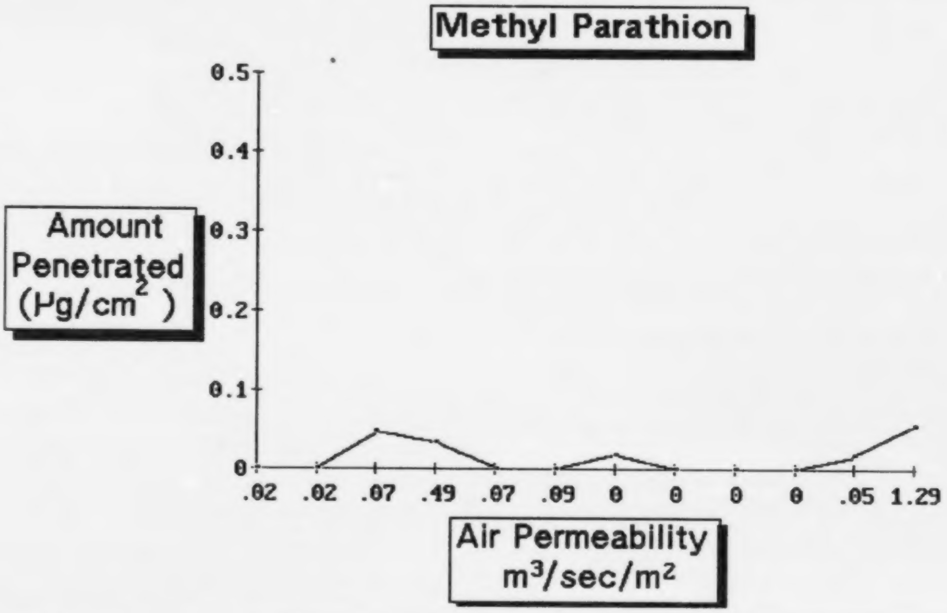


Figure 9. (continued)

excellent protection for three of the pesticides, but only average protection with the fourth pesticide, Captan. This fabric was a composite made of a layer of polytetrafluoroethylene (PTFE) between a woven and knitted layer. The PTFE is thought to be the primary reason for this fabric's performance. The fact that only average protection was provided for the pesticide Captan was not expected and is thought to be due to the nature of the pesticide solution.

Treated and untreated denim fabrics, had the next lowest air permeability ratings and provided excellent protection from three of the four pesticides and medium to good protection from the pesticide Captan. The twill fabrics had the third lowest air permeability ratings and also provided excellent protection from three of the four pesticides and good protection from the fourth pesticide, Captan.

Treated and untreated chambray, had medium air permeability ratings, and penetration occurred for all four pesticides. The fabric which had the highest air permeability ratings also provided only average to poor protection for all four pesticides.

Therefore, the study concluded that the actual air permeability numbers did not correlate with the degree of penetration. However, it is important to note that the range of penetration that occurred for all fabrics was small. Seventy-three percent of the fabrics had less than .025 $\mu g/cm^2$ pesticide penetration. Air permeability values for the fabrics ranged from 0.0 $m^3/sec/m^2$ to 1.29 $m^3/sec/m^2$. Eighty-three percent of the fabrics had values less than .10 $m^3/sec/m^2$. Had there been a better distribution across the range of penetration and air permeability, better correlation between air permeability and pesticide penetration might have been achieved.

Fabric Construction--

The construction classification was based on the method used to form the fabric (Table 5). These classes are woven and nonwoven. Because of the differences in characteristics of the classes of woven and nonwoven fabrics, comparisons were made within each class. Fabric construction did significantly influence pesticide penetration.

Nonwoven Fabrics--The untreated nonwoven, 100% spun-bonded olefin Tyvek®allowed penetration of Methyl Parathion and Captan and provided the greatest protection from Ethion and Dicofol. Two of six nonwoven fabrics (Saranex and polyethylene-coated Tyvek®) provided protection against detectable penetration for all pesticides used in the study. Both were 100% spun-bonded olefin fabrics with impermeable coatings. These results matched expectation. The composite Gore Tex® fabric provided protection against three of the pesticides but provided below average for the pesticide Captan. This composite contains a microporous layer of PTFE, which has many tiny holes that allow only air to pass through. Therefore, it is theorized that the pesticide particles were stopped by this layer for three pesticides. However, penetration by the Captan was not expected. It is believed that penetration of the Captan results from the nature of the pesticide solution and may be a result of inert ingredient, since Captan had higher penetration values for all fabrics tested.

The composite nonwoven, spunbonded/meltblown/spunbonded (Ex. 1), provided protection from two pesticides, but only average protection from Methyl Parathion and Captan. It was expected that this fabric would provide excellent protection in all cases because of the fabric formation. Meltblown fabrics are produced using microfibers which are considered to have excellent filtering potential. The fibers are actually trapping the pesticide in the fabric and thus, prevents movement through the fabric.

The nonwoven fabric (Ex. 2) provided poor to average protection for all pesticides. In each case, this fabric did allow some penetration of pesticide. This fabric is a point-bonded nonwoven with polyester binder fibers. This fabric was experimental and not originally intended for protective clothing.

Woven Fabrics--Six woven fabrics were included in the study. These were treated (fluorocarbon finish) and untreated samples of the same base fabrics. Four were a 2 x 1 twill construction and two fabrics were of a plain weave. The plain weave was much lighter in weight and lower in thickness than the twill weave fabrics (Table 5).

The treated and untreated plain weave fabrics, allowed penetration of all four pesticides. The twill fabrics permitted penetration only of the pesticide Captan and were ranked above average and below average. The treated denim and twill fabrics did not provide increased protection when compared with the untreated denim and twill fabrics.

The finding that the plain woven fabrics allowed more penetration than the twill fabrics indicated that fabric construction has an influence on the ability of the fabric to prevent pesticide penetration. However, the weight and thickness of the twill fabrics were higher than plain woven fabric. Therefore, the difference in performance of the fabrics cannot be attributed to construction alone

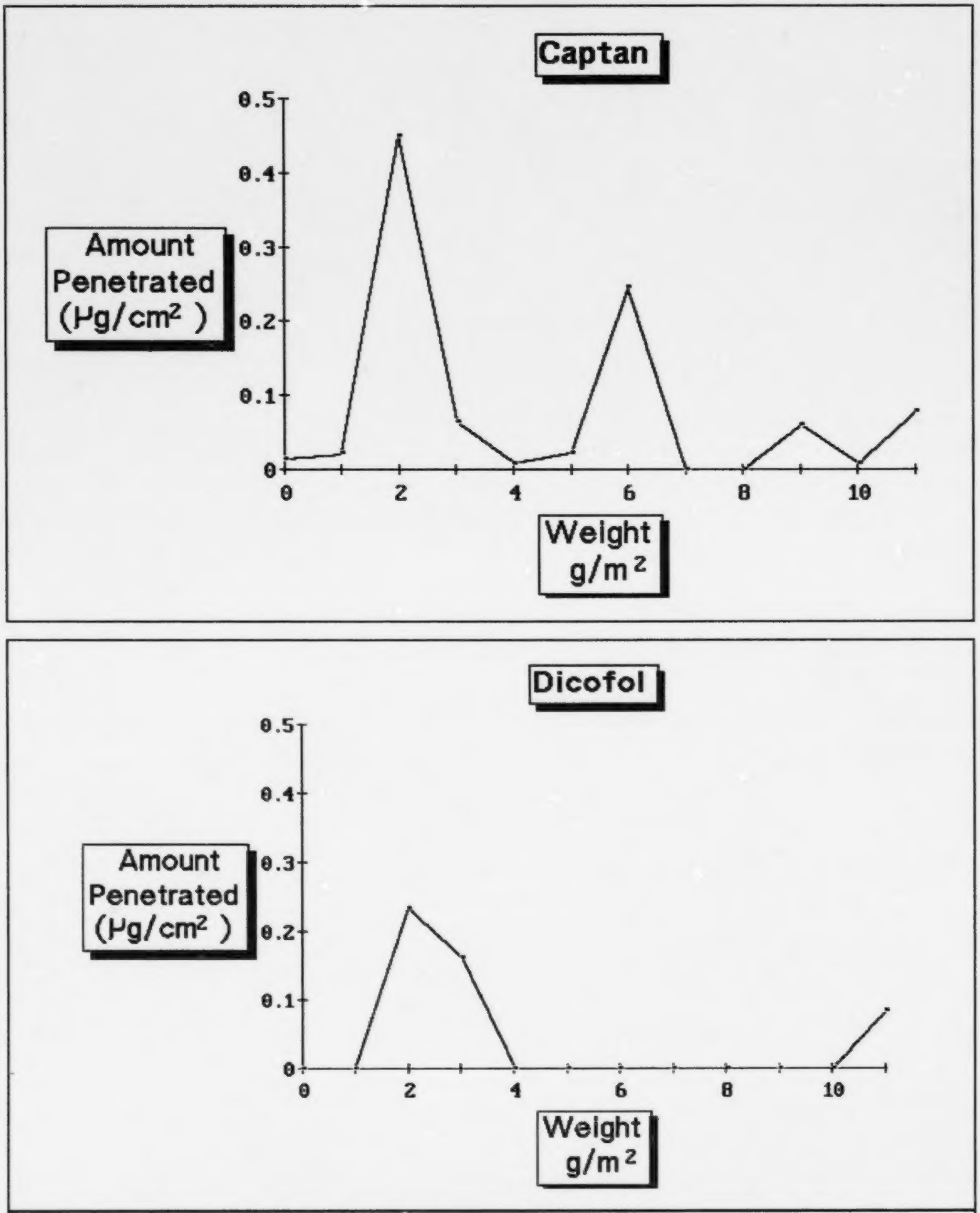


Figure 10. Weight vs. Penetration for Untreated Fabrics

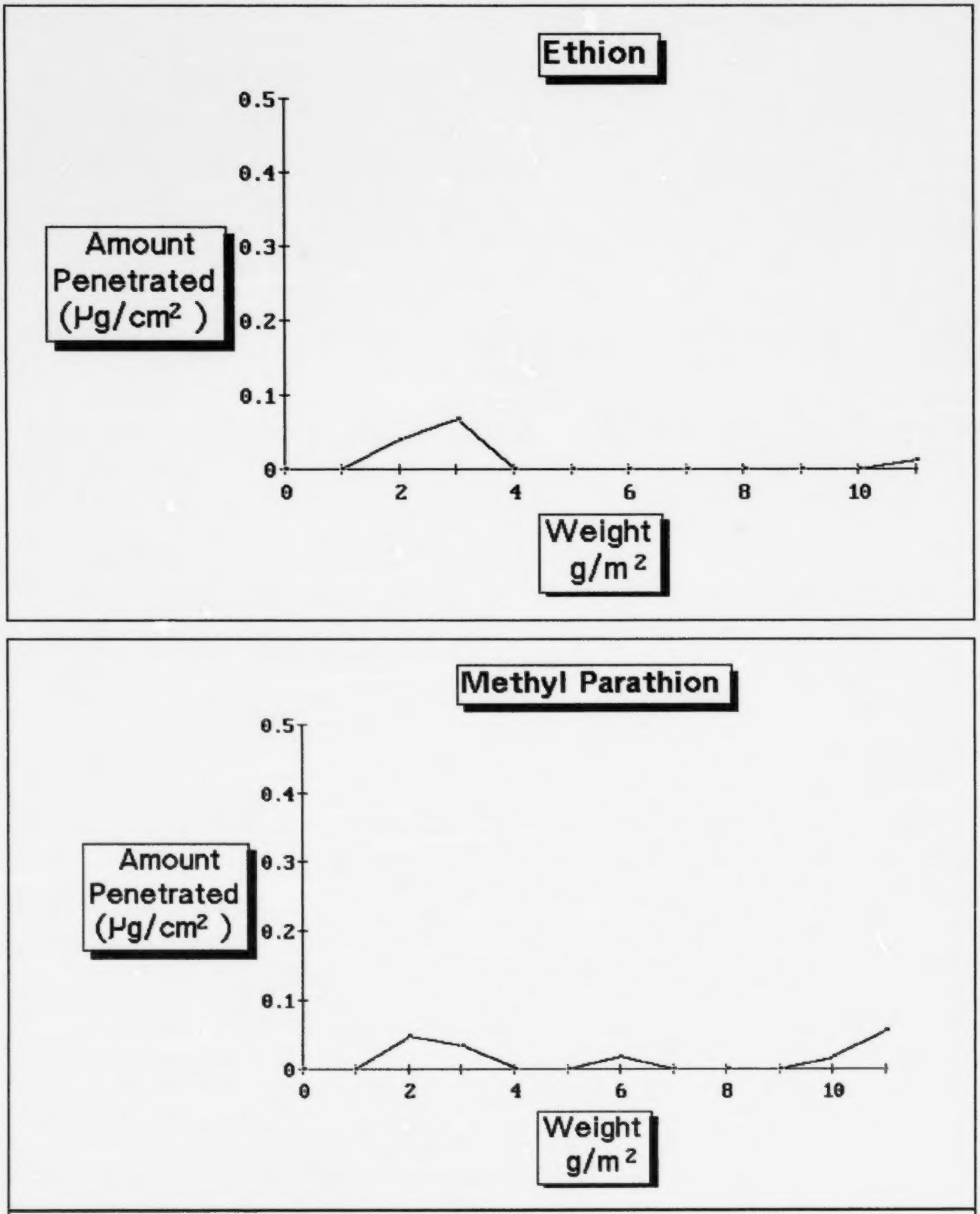


Figure 10. (continued)

because of the interaction of weight and thickness. A trend is observed for decreased penetration as weight increases (Figure 10).

Fiber Content--

The physical and chemical properties of the fiber also influence the fabric's ability to prevent penetration. If the fiber is smooth and has a round cross-section, as commonly found in synthetic fibers, the pesticide particle may slide around the fiber and cause continuous traveling through the fabric. Convolutions as found in cotton fiber can trap the particle in the natural twists and thus prevent further movement. The chemical nature of the fiber dictates the hydrophilic and oleophilic characteristics of the fiber. The hydrophilic fibers absorb the water, while the oleophilic absorb oil. An oil-based pesticide may be absorbed into the synthetic fibers and thus eliminate further movement and penetration. Although the physical and chemical properties may account for some of the variations found in fiber content, they were not a significant factor in controlling penetration in this study. This was probably due to the interaction of the fabric variables: weight, thickness, construction, and surface characteristics.

Table 10. GENERAL LINEAR MODEL: INITIAL STUDY

Pesticide	Variable	% of Total
Captan	Thickness	13.99
	Air permeability	3.22
	Weight	0.19
	Surface energy	20.99
	Spray rating	0.07
Dicofol	Thickness	13.10
	Air permeability	4.54
	Weight	2.99
	Surface energy	1.98
	Spray rating	0.11
Ethion	Thickness	16.52
	Air permeability	5.35
	Weight	2.93
	Surface Energy	3.50
	Spray rating	2.45
Methyl Parathion	Thickness	27.40
	Air permeability	14.26
	Weight	6.11
	Surface energy	0.62
	Spray rating	0.38

Overall Contribution of Fabric Characteristics to Penetration

Using the general linear model for statistical analysis procedure, it was possible to determine what percentage selected characteristics contributed to the overall performance of the fabric as a barrier to pesticide penetration. Table 10 shows these characteristics and the percent of their contribution. Only continuous variables of weight, thickness, air permeability, surface energy, and spray rating were included in this model. The categorical variables of fabric construction, fiber content, and finish were excluded.

The variables of thickness and air permeability contributed from 13% to 27% of the total for all four pesticides. As the fabric thickness increased, pesticide penetration decreased because penetration is a function of distance, and thickness is the distance the pesticide must travel to penetrate the fabric. Air permeability measures a fabric's resistance to air. The higher the air permeability measurement, the more porous the fabric. The more porous fabrics allowed greater penetration of the pesticide for the woven fabrics tested in this study. The results were not always the same for the nonwoven fabrics.

The contribution of the remaining measurable independent variables--weight, surface energy, and spray rating--was less than 9%. The only exception was for the pesticide Captan, where surface energy accounted for 21% of the total. Surface energy and spray rating measure the repellency of the fabric. These variables had little influence on the amount of pesticide that penetrated each fabric-an indication that these are not accurate measurements of penetration that might occur through a specific fabric. The exception that occurred for surface energy, the pesticide Captan, may be due to the nature of the pesticide solution. Fabric weight also did not contribute to the overall performance of the fabric. A fabric's weight is dependent on many different fabric properties, including fiber content, finish, and construction. The weight of the woven fabrics was highly correlated with thickness; as weight increased, thickness increased. This correlation did not exist for the nonwoven fabrics, due to varying construction techniques and surface treatments which greatly influenced fabric weight.

The amount not identified by the variables included in the GLM model is thought to be due to variations in construction, surface treatments, and fiber content. Differences between the performance of the untreated woven and nonwoven fabrics were evident. Two of the woven fabrics (denim and twill) allowed less pesticide penetration than the nonwoven fabric (Tyvek®). The woven fabrics of twill construction (denim and twill) allowed less penetration than the fabric of plain construction (chambray).

Surface treatments did not consistently reduce the amount of penetration that occurred when compared with fabrics that had no surface treatment. The impermeable coatings eliminated penetration, and the repellent finishes either reduced, did not change, or increased the amount of penetration that occurred.

Due to the many variables being examined, the effect of fiber content could not be isolated for the fabrics. Although the influence contributed to the overall performance of the fabric, the exact amount could not be identified in this study.

Conclusion

Fabrics of different construction and fiber content provide varying degrees of protection against pesticide penetration as applied in spray form. This was an exploratory investigation to determine the influence of fabric characteristics on pesticide penetration through fabrics and was not in-depth enough to isolate more than trends. Fabric characteristics of thickness, air permeability, weight, finish, and fiber content may be valuable indicators of fabric penetration performance. Fabrics with surface treatments designed to increase repellency did not consistently aid in the reduction of pesticide penetration. For the woven fabrics, it was concluded that the fabric characteristics thickness and weight contributed to the ability of a fabric to prevent pesticide penetration. For woven fabrics, the greater the fabric thickness, the better protection that was provided. In all cases weight increased as thickness increased causing an experimental interaction that could not isolate either characteristic.

There was a trend indicating that penetration could also be predicted by air permeability for woven fabric structures. As the air permeability of the fabric increased, the likelihood of penetration increased, but only for woven fabrics. The fabric characteristics of surface energy and spray rating could not be used to predict penetration.

The fabrics analyzed for this study were chosen because they are used in garments readily available to agriculture workers. This type of study allowed for a benchmark of currently available garments; however, this approach did not allow for direct comparisons of single fabric variables (i.e. weight was not held constant while thickness varied). The research identified the need to clarify these variables in the next phase of this research.

EFFECT OF FABRIC WEIGHT AND THICKNESS ON PESTICIDE PENETRATION

Agricultural workers have identified denim jeans and woven coveralls as preferred apparel for pesticide application because most of the nonwoven fabrics currently available are uncomfortable in hot weather (10). Fabrics previously evaluated for pesticide penetration were chosen because of their availability and common use by agricultural workers (11). Laboratory evaluation of these fabrics has determined that both measurable and categorical variables of fabric characteristics may influence penetration. The results were that nonwoven fabrics provided the best protection against the penetration of pesticides. However, woven fabrics of heavy weight twill construction, including denim, performed considerably well against the penetration of pesticides. The extremes of woven fabrics, from a light-weight work shirt to a heavy-weight denim, were evaluated. As expected, the heavier-weight fabrics performed better than the light weight. The question arises as to how heavy does a woven fabric have to be to provide comparable protection to the nonwoven fabrics. In addition, as denim and heavy-weight twill are worn, the fabric wears and becomes lighter in weight. It is not uncommon for a 472 g/m^2 (14 oz/yd^2) denim pant to become 270 g/m^2 (8 oz/yd^2) after washing and wearing. Because most of the studies conducted to date have been on new commonly worn fabrics, no information is available on how penetration is affected as fabric weight and thickness decrease. The purpose of this study was to evaluate the effect of fabric weight and thickness of woven fabrics on pesticide spray penetration. Fabrics were specifically selected to represent various levels of the variables for comparison.

Methodology

Fabrics--

Eight fabrics of 100% cotton or 50/50% cotton/polyester were pre-laundered using an adaptation of AATCC Test Method 135: "Dimensional Changes in Automatic Home Laundering of Woven and Knit Fabrics" (see Appendix A). The fabrics then were characterized by measuring the weight and thickness.

The fabric thickness was determined in accordance with ASTM Test Method D-1777. A 7.62 cm square sample was cut and conditioned. The thickness was then determined using an Ames Thickness Gauge. The procedure was repeated five times and the mean and standard deviation calculated. The mean was used to represent each fabric.

The weight of the fabrics was obtained using a Mettler Model H Balance in accordance with ASTM Test Method D-3776. Five by five centimeter samples were weighed and the results converted to g/m^2. The mean of five replications was taken and used to represent each fabric.

The eight fabrics selected were then finished with a fluorocarbon treatment for a total of 16 fabrics (Table 11). In addition, four carry over fabrics were included for validation of the experimental design. Weights varied from 497.01 g/m^2 (14.64 oz/yd^2) to 99.86 g/m^2 (2.94 oz/yd^2) (Table 12). Thickness varied from .8636 mm (.0366 in) to .2489 mm (.008 in). Figure 11 and 12

Table 11. FABRIC DESCRIPTION: WEIGHT & THICKNESS STUDY

Code	Common Name	Fiber Content	Construction	Finish
W1	Poplin	100% cotton	Plain Weave	UF[+]
W2	Poplin	100% cotton	Plain Weave	F[++]
W3	Broadcloth	100% cotton	Plain Weave	UF
W4	Broadcloth	100% cotton	Plain Weave	F
W5	Broadcloth	100% cotton	Plain Weave	UF
W6	Broadcloth	100% cotton	Plain Weave	F
W7	Duck	100% cotton	Plain Weave	UF
W8	Duck	100% cotton	Plain Weave	F
W9	Print Cloth	50/50 cotton/polyester	Plain Weave	UF
W10	Print Cloth	50/50 cotton/polyester	Plain Weave	F
W11	Twill	100% cotton	Twill Weave	UF
W12	Twill	100% cotton	Twill Weave	F
W13	Twill	100% cotton	Twill Weave	UF
W14	Twill	100% cotton	Twill Weave	F
W15	Twill	50/50 cotton/polyester	Twill Weave	UF
W16	Twill	50/50 coton/polyester	Twill Weave	F
W25	Denim	100% cotton	Twill Weave	UF
W23	Chambray	100% cotton	Plain Weave	UF
N1	Tyvek®	100% polypropylene	Nonwoven	UF
N7	SMS	100% polypropylene	Nonwoven	UF

[+] UF - Unfinished

[++] F - Fluorocarbon Finish

Table 12. CHARACTERISTICS OF WOVEN FABRICS

Fabric	Thickness mm	Weight g/m^2	Air Permeability $m^3/sec/m^2$	Spray Rating	Yarn Count warp	fill
W1	.46	250.32	.03	0	112.13	54.5
W2	.38	250.32	.06	100	112.13	54.5
W3	.28	121.01	.22	0	141.70	62.6
W4	.25	123.97	.37	100	141.70	62.6
W5	.24	99.86	.22	0	72.0	72.0
W6	.20	107.12	.34	92	72.0	72.0
W7	.69	401.20	.01	0	58.5	44.1
W8	.56	401.20	.020	100	58.5	44.1
W9	.28	105.67	1.11	0	88.2	54.6
W10	.25	105.67	1.20	100	88.2	54.6
W11	.66	234.18	.39	0	96.9	43.7
W12	.48	234.18	.34	100	96.9	43.7
W13	.93	494.16	.17	0	69.6	52.5
W14	.84	495.16	.02	100	69.6	52.5
W15	.86	493.86	.02	0	75.2	52.0
W16	.84	497.01	.04	100	75.2	52.0
W23	.43	173.05	.23	50	36.03	26.7
W25	.69	267.26	.13	0	70.7	48.5

Thickness - ASTM D1777-64

Weight - ASTM D3776-79

Air Permeability - ASTM D3737-75

Spray Rating - AATCC 22-1980

Yarn Count - ASTM D3775-79

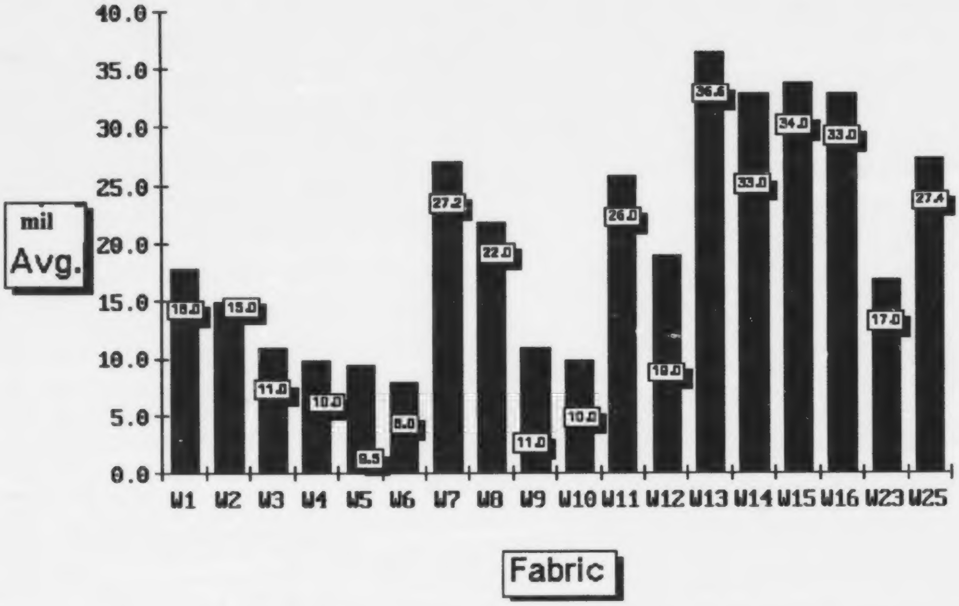


Figure 11. Woven Fabric Thickness

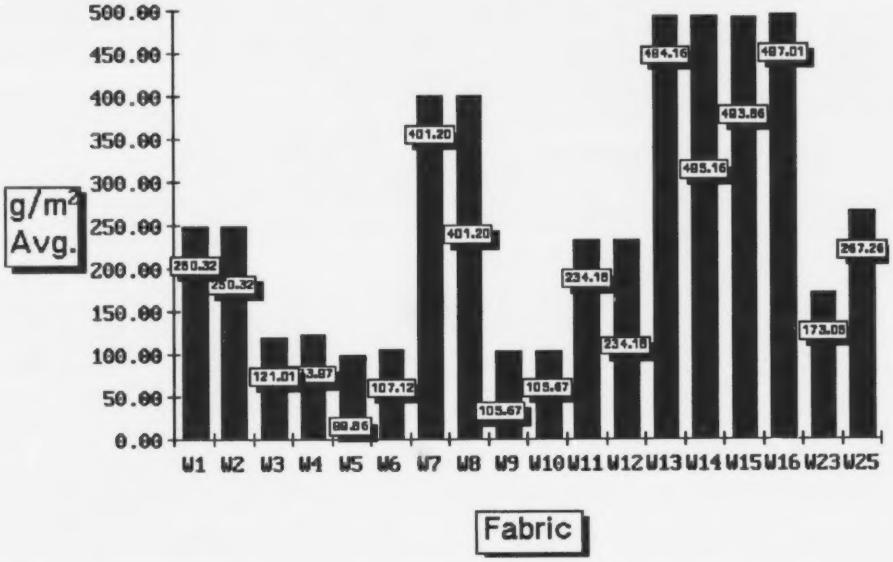


Figure 12. Woven Fabric Weight

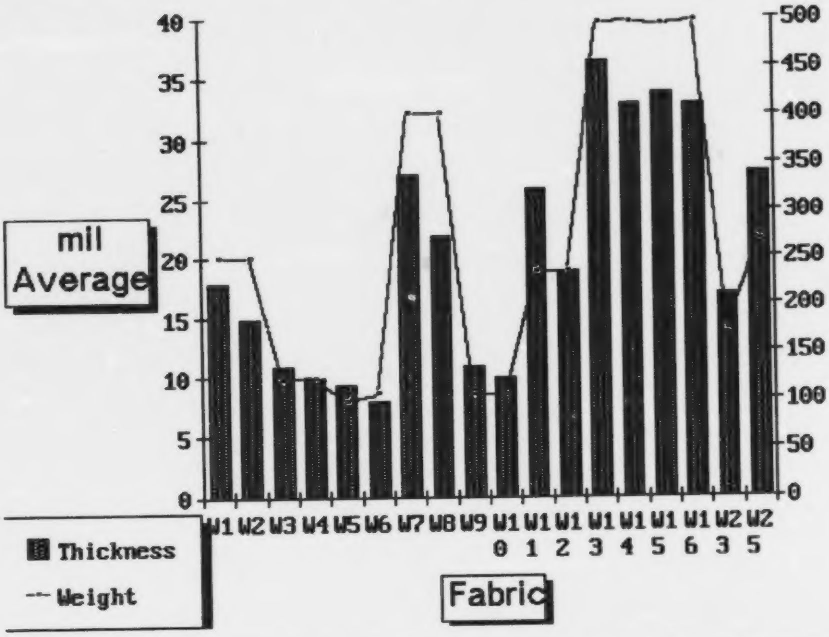


Figure 13. Woven Fabrics Compared by Weight and Thickness

illustrate thickness and weight of the 18 fabrics. These two characteristics are related (Figure 13): as thickness increases there is a corresponding increase in weight.

Exposure--

The pesticides were selected to correlate with the pesticides used in field studies. Three pesticides were evaluated: Ethion (46.5% active ingredient), Chlorobenzilate (45.5% active ingredient), and Dicofol (42% active ingredient). An emulsifiable concentrate formulation of each chemical was used to prepare a 0.12% solution. For exposure, the fabrics were incorporated into a multi-layer fabric assembly. The top layer was the fabric being evaluated. An inner layer of 50/50 cotton/ polyester jersey knit forms the collector layer beneath which a foil layer served to collect any pesticide that penetrated through the two upper layers and an additional foil layer that served as a splash layer. The layers were combined using standard sampling preparation procedures (see Appendix A). The fabrics were numbered and a random order determined statistically for the exposure process (see Appendix C).

The exposure took place in an enclosed spray chamber that was designed to simulate field conditions using standard procedures (see Appendix A). The fabrics were removed from the chamber and allowed to dry for one hour. Temperature and humidity were maintained at 22°C and 65% relative humidity during the exposure and drying. After drying, a swatch was cut from the center of the collector layer of each specimen and extracted according to standard procedures (see Appendix A). A randomly selected 20% of the fabrics also had a swatch removed from the test fabric and inner foil layer to be analyzed for quality control. Extracts were analyzed by gas chromatography (see Appendix B).

Results and Discussion

Pesticide Penetration Through Fabrics--

Other research studies have shown that fabric variations allowed variable amounts of pesticide penetration. As Table 13 illustrates, the same is true in this research. The characteristics of fabric weight and thickness closely parallel penetration results (Figure 14, 15, and 16). Combined results

Table 13. PESTICIDE PENETRATION THROUGH WOVEN FABRICS

		Pesticide Penetration µg/cm^2					
Code	Fabric	Chlorobenzilate	SD	Dicofol	SD	Ethion	SD
W1	Poplin	(5) ND	.000	(5) .004	.001	(5) ND	.000
W2	Poplin	(5) ND	.000	(5) .017	.034	(5) ND	.000
W3	Broadcloth	(5) .115	.057	(5) .049	.011	(5) .101	.041
W4	Broadcloth	(5) .114	.043	(5) .103	.114	(5) .102	.042
W5	Broadcloth	(5) .124	.046	(5) .097	.067	(5) .101	.034
W6	Broadcloth	(5) .119	.047	(5) .100	.041	(5) .084	.020
W7	Duck	(5) ND	.000	(5) .002	.003	(4) ND	.000
W8	Duck	(5) ND	.000	(5) .001	.002	(5) ND	.000
W9	Print Cloth	(5) .468	.053	(5) .346	.049	(5) .481	.180
W10	Print Cloth	(5) .350	.048	(5) .269	.060	(5) .356	.199
W11	Twill	(5) ND	.000	(5) .004	.008	(5) ND	.000
W12	Twill	(5) ND	.000	(5) ND	.000	(5) ND	.000
W13	Twill	(5) ND	.000	(5) .004	.003	(5) ND	.000
W14	Twill	(5) ND	.000	(5) ND	.000	(5) ND	.000
W15	Twill	(5) ND	.000	(5) .013	.003	(5) .015	.014
W16	Twill	(5) .027	.037	(5) .015	.022	(5) .033	.011
W23	Chambray	(5) .038	.052	(5) .015	.021	(5) .037	.008
W25	Denim	(5) ND	.000	(5) ND	.000	(5) ND	.000
N1	Tyvek®	(5) ND	.000	(5) ND	.000	(5) ND	.000
N7	SMS	(5) .016	.035	(5) ND	.000	(5) ND	.000

ND -- non detectable
(#) -- number of replications
SD -- standard deviation

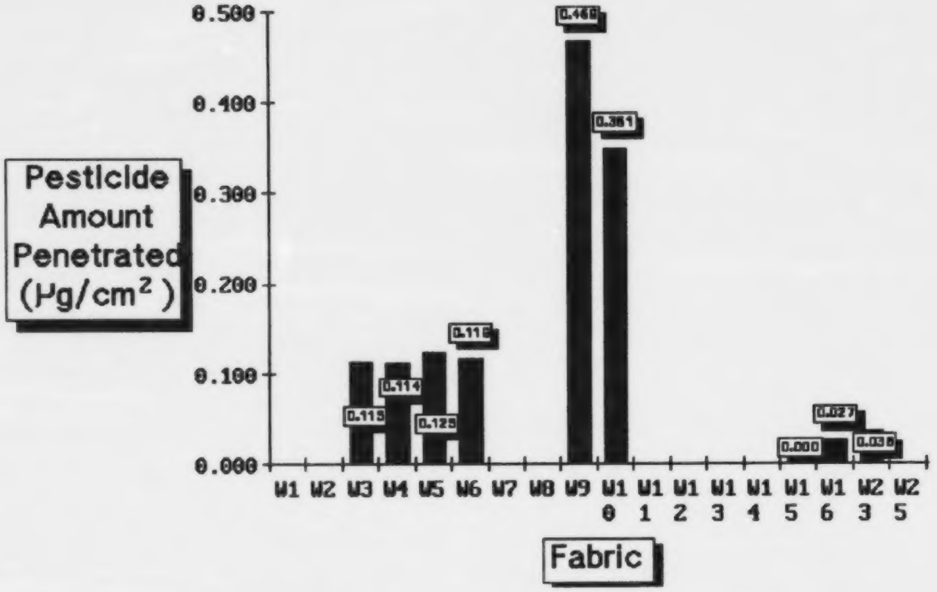


Figure 14. Fabric Pesticide Penetration - Chlorobenzilate

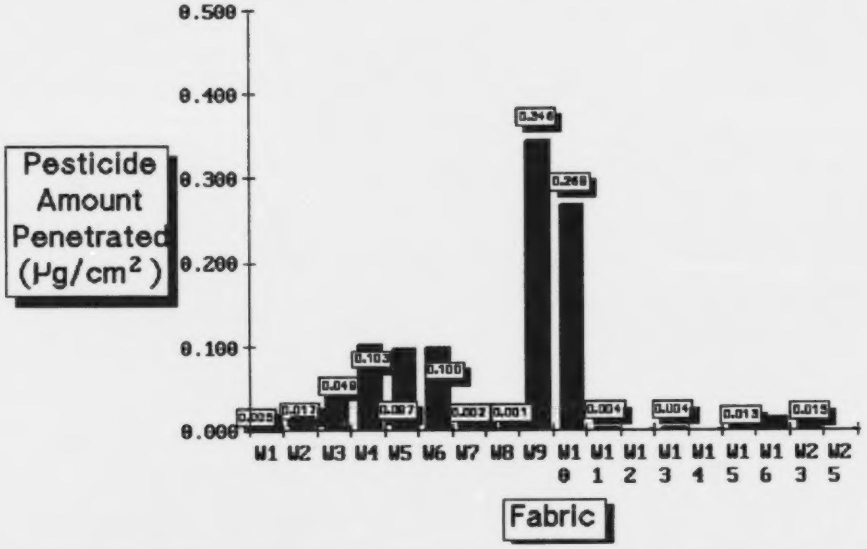


Figure 15. Fabric Pesticide Penetration - Dicofol

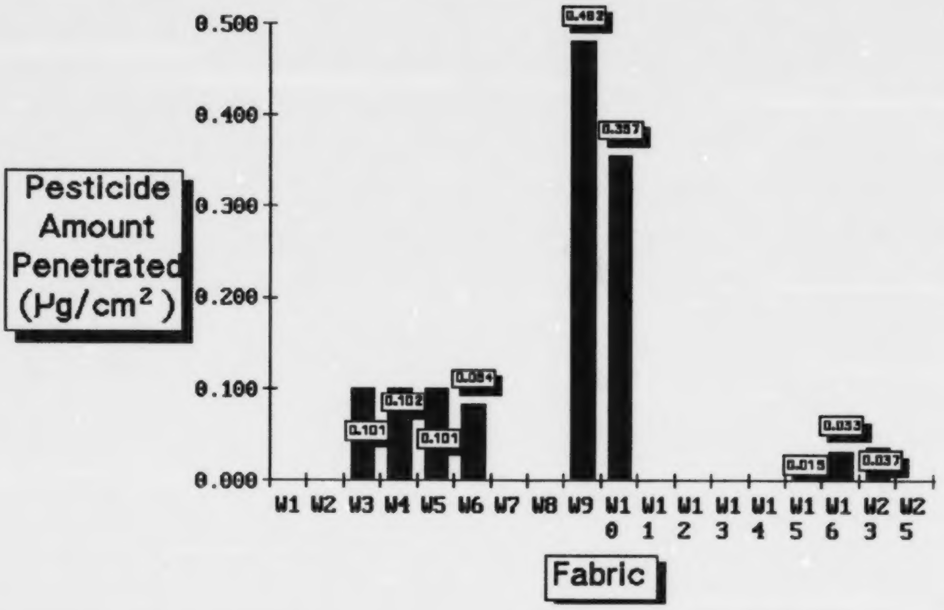


Figure 16. Fabric Pesticide Penetration - Ethion

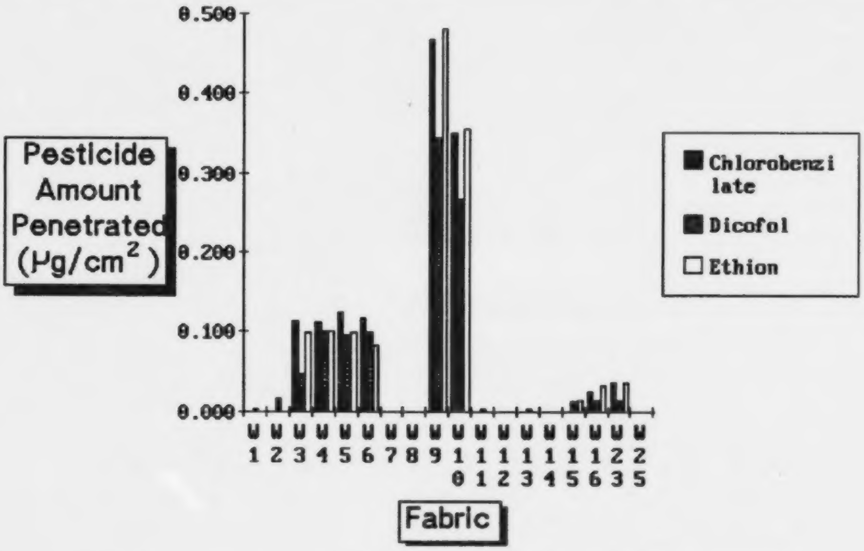


Figure 17. Comparison of Pesticide Penetration

of all three pesticides illustrate variances in penetration are more closely related to fabric weight and thickness than type of pesticides (Figure 17).

Duncan's multiple range test grouped the fabrics according to the amount of pesticide penetration through fabrics. The results showed three distinct grouping of fabrics (Tables 14-16). The mean penetrations for each fabric of each group then were combined into a group mean and graphically illustrated (Figures 18, 19, and 20). Group 1 included fabrics in which all 5 replications within each fabric type allowed penetration. The fabrics in sub-group A,B allowed the greatest penetration or would provide the least protection. Group 3 included fabrics in which all 5 replications within each fabric type allowed no detectable penetration of pesticides through the fabrics. However, the fabrics within Group 2 were not as clearly defined. For example, for the pesticide Chlorobenzilate, fabric #20 had four replications for which no detectable (ND) penetration was found. However in one at least one replication measurable amounts of residue were detected. Statistically, the data excluding the zeros, was analyzed and then reanalyzed to include all five replications , for purposes of calculating the mean and grouping the results for comparisons (see Appendix C).

Table 14. DUNCAN'S MULTIPLE RANGE TEST -CHLOROBENZILATE

	Groupings	Mean ($\mu g/cm^2$)	Fabric
Group 1	A	.468	W9
	A	.350	W10
	B	.124	W5
	B	.119	W6
	B	.115	W3
	B	.114	W4
Group 2	C	.038	W23
	C	.027	W16
	C	.016	N7
Group 3	D	ND	W1
	D	ND	W2
	D	ND	W7
	D	ND	W8
	D	ND	W8
	D	ND	W11
	D	ND	W12
	D	ND	W13
	D	ND	W14
	D	ND	W15
	D	ND	W25
	D	ND	N1

ND non detectable

Table 15. DUNCAN'S MULTIPLE RANGE TEST - ETHION

	Groupings	Mean ($\mu g/cm^2$)	Fabric
	A	.481	W9
	A	.356	W10
Group 1	B	.101	W5
	B	.102	W4
	B	.101	W3
	B	.084	W6
	C	.037	W23
Group 2	C	.033	W16
	C	.015	W15
	D	ND	W1
	D	ND	W2
	D	ND	W7
	D	ND	W8
	D	ND	W11
Group 3	D	ND	W12
	D	ND	W13
	D	ND	W14
	D	ND	W25
	D	ND	N1
	D	ND	N7

ND non detectable

Table 16. DUNCAN'S MULTIPLE RANGE TEST - DICOFOL

	Groupings	Mean (μg/cm^2)	Fabric
Group 1	A	.346	W9
	A	.269	W10
	B	.103	W4
	B	.100	W6
	B	.097	W5
Group 2	C	.049	W3
	D	.017	W2
	D	.015	W16
	D	.015	W23
	D	.013	W15
	D	.004	W1
	D	.004	W11
	D	.004	W13
	D	.002	W7
	D	.001	W8
Group 3	E	ND	W12
	E	ND	W25
	E	ND	N7
	E	ND	W14
	E	ND	N1

ND non detectable

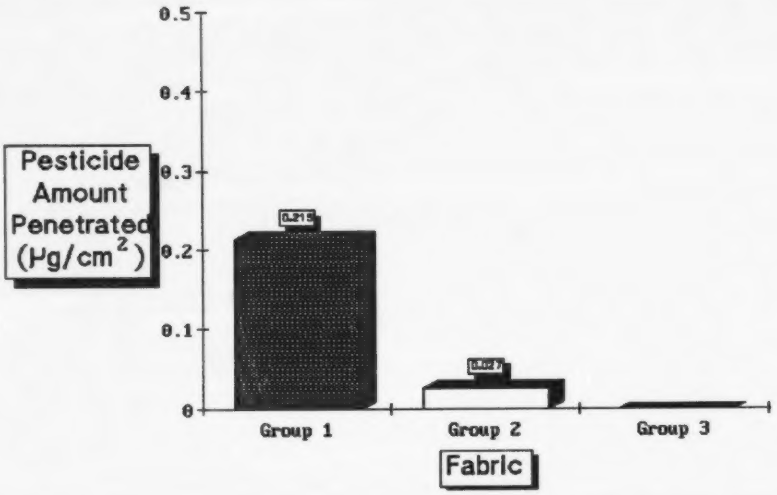


Figure 18. Duncan's Multiple Range Test - Chlorobenzilate

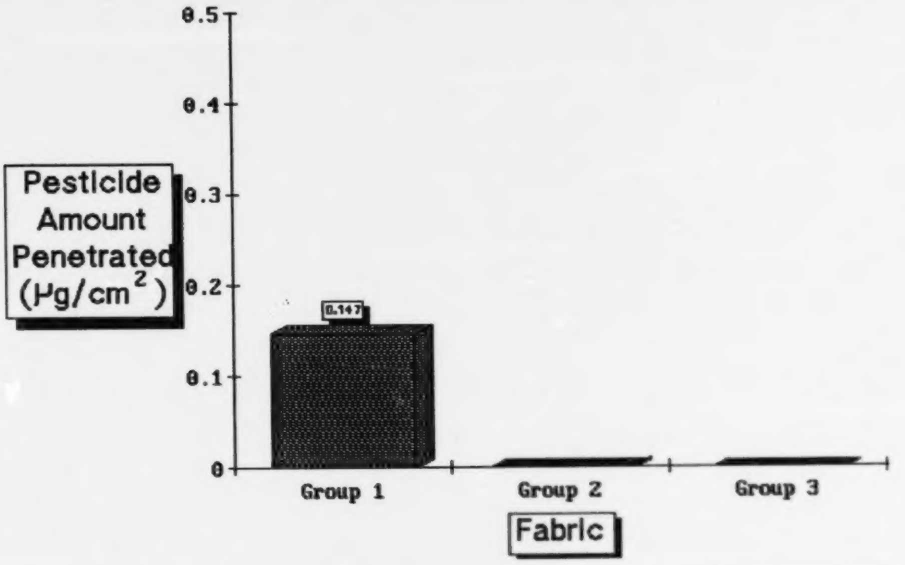


Figure 19. Duncan's Multiple Range Test - Ethion

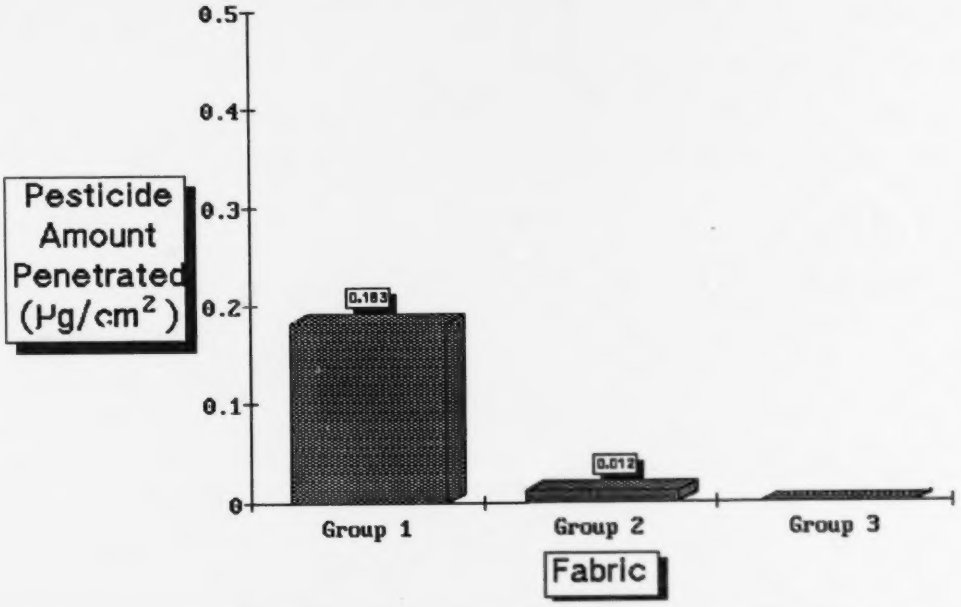


Figure 20. Duncan's Multiple Range Test - Dicofol

Fabric Finish--

Fabric finish did not statistically affect the ability of a fabric to provide protection for pesticide penetration. This may be attributed to the procedure used for sample exposure (see Appendix B). In this study, the fabric samples were sprayed at a 90° angle to the spray then fabrics were removed from the spray chamber and allowed to dry for one hour in the horizontal position. Therefore, the pesticide solution remained on the surface of the test fabric, either as a wetted-out fabric or a beaded liquid solution. After the 60 minute drying time, the fabrics were considered dry. It is possible that over time (one hour) the protection initially produced by the finish was lost. A change in surface energies or evaporation of the liquid or migration of the pesticide into the capillary size opening in the finished fabrics may have been the cause. Additional research is needed to explain this result. However, this discovery may explain why finishing the fabrics did not alter protection in this study and may correlate to the type of exposure a tractor operator experiences in the thigh area or to other body parts that are wetted out or exposed to pesticide spray during the field application.

Fabric Weight--

The fabric characteristic of weight was shown to be highly correlated with penetration. As weight decreased pesticide penetration increased. In the original analysis weight was analyzed as a class variable (low, medium, and high) showing the relationship of weight to penetration. However, when efforts were made to plot the best fitting line, it was skewed either upward or downward depending on the presence of cotton/polyester blended fabrics. Therefore, the decision was made to investigate the effect of weight and to hold all other variables constant. The results shown in Figures 21, 22 and 23 illustrate the relationship of weight for 100% cotton, plain weave,

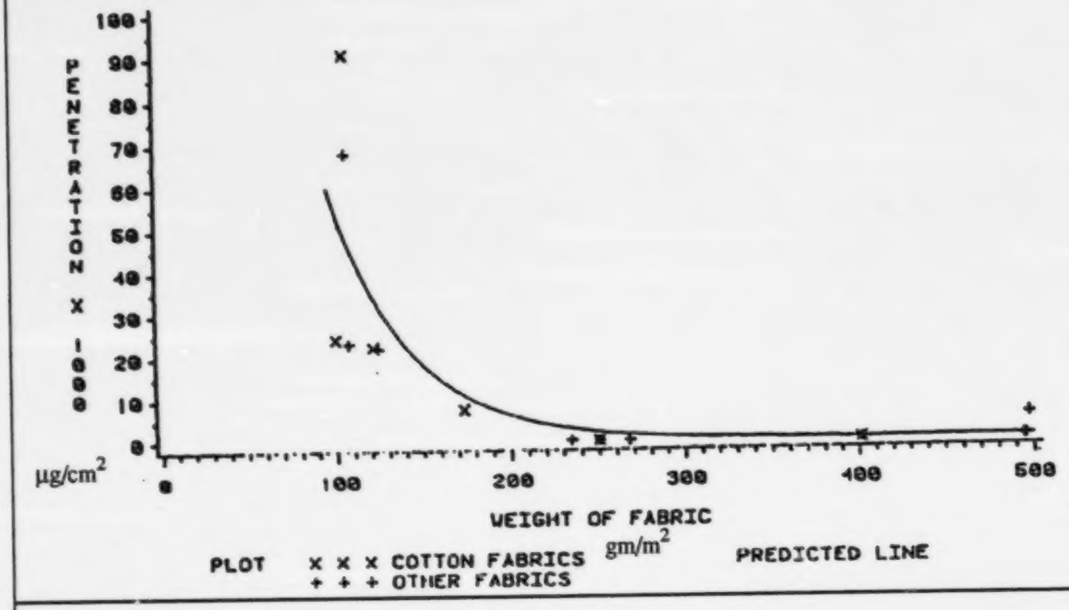


Figure 21. Regression Line Unfinished Fabric:Chlorobenzilate

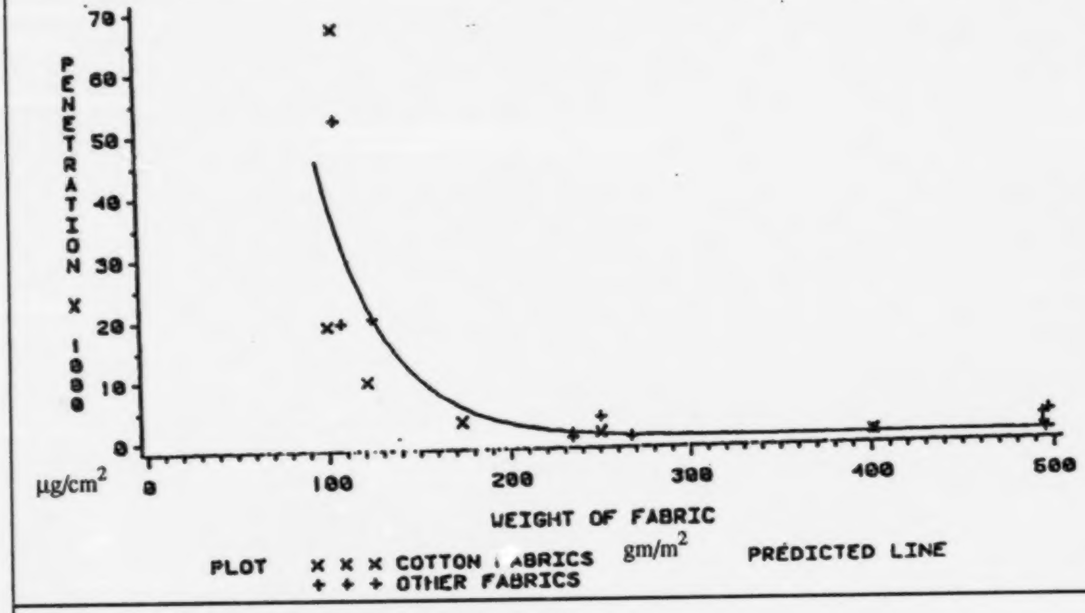


Figure 22. Regression Line Unfinished Fabric: Dicofol

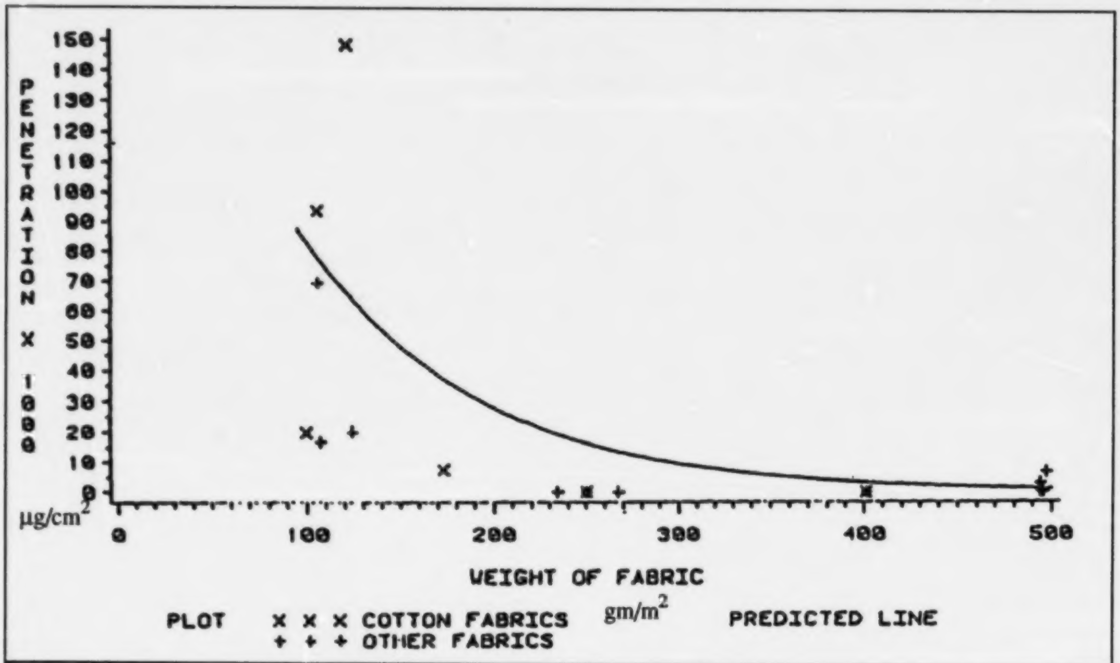


Figure 23. Regression Line Unfinished Fabric: Ethion

unfinished fabrics. The means for all other fabrics have been charted on the graph to show their relationship to this curve.

This illustrates a problem that may not have been taken into account by previous research. The effect of fabric variables such as weight cannot be analyzed unless all other variables i.e., fiber content, fabric construction and finish are held constant.

Fabric Thickness--

In the statistical analysis the general linear model examined the effect of "thickness" as a class variable given weight and weight given thickness. The results showed that weight and thickness were confounded and could not be separated in this particular study. The low thickness fabrics are also the low-weight fabrics and the high-thickness fabrics are the heavier weights (Table 12). Therefore, a graph of thickness versus penetration would have the same curve or relationship as weight versus penetration. To isolate completely the effects of thickness or weight, a fabric should be engineered with low weight and high thickness or heavy weight and low thickness. There are fabrics available that would enable research to isolate weight and thickness as independent variables; however these fabrics are not practical to consider for effective barriers in penetration.

Conclusions

This phase of the study concluded that for woven fabrics the effects of weight and thickness were confounded, and thus were not separated in this study. However, if thickness remains the same, penetration may be attributed to fabric weight. As fabric weight increases, penetration decreases.

This study isolated the influence of weight and thickness on pesticide penetration. The findings show that fabrics under 250 g/m^2 (7.37 oz./yd.^{2}) could be vulnerable to greater amounts of penetration.

The overall conclusions drawn from this phase of the study are that agricultural workers should avoid wearing medium to light-weight woven clothing if they are applying pesticides, or avoid wearing clothing that has been reduced from its initial weight by wearing and washing after it has reached the category of medium weight or below.

Conclusions

This phase of the study concluded that for woven fabrics the effects of weight and thickness were confounded, and thus were not separated in this study. However, if thickness remains the same, penetration may be attributed to fabric weight. As fabric weight increases, penetration decreases.

This study isolated the influence of weight and thickness on pesticide penetration. The findings show that fabrics under 250 g/m^2 (7.37 $oz./yd.^2$) could be vulnerable to greater amounts of penetration.

The overall conclusions drawn from this phase of the study are that agricultural workers should avoid wearing medium to light-weight woven clothing if they are applying pesticides, or avoid wearing clothing that has been reduced from its initial weight by wearing and washing after it has reached the category of medium weight or below.

EVALUATION OF NONWOVEN FABRICS AS BARRIERS TO PESTICIDE

Nonwoven fabrics are available as protective barriers to pesticide penetration. Most of the protective suits on the market are made of the fabric Tyvek®.

In previous studies this fabric has proved to be an effective barrier to pesticide penetration, especially when Tyvek® has been coated with either a Saranex® or a polyethylene coating. However, the thermal comfort field tests that have been conducted on Tyvek® have shown that it is very uncomfortable in temperatures greater than 29°C (12). Therefore, alternative nonwoven fabrics have been marketed with claims not only of protection from small particulates, such as pesticides, but also of thermal comfort even in extreme weather conditions. The purpose of this study was to evaluate the performance of a range of nonwoven fabrics as barriers to pesticide penetration.

Fabrics

Traditional nonwoven fabrics, such as treated and untreated Tyvek®, were included in the previous study which also evaluated two additional nonwoven fabrics. In addition, both currently available and experimental fabrics were selected to be evaluated (Table 17). The fabrics were either finished or unfinished. The finished fabrics were treated with a fluorochemical treatment either on one or both sides of the fabric.

Exposure and Analysis

The procedures for exposure, extraction, and analysis were the standard procedures developed earlier in this research project (Appendix A and B).

Results and Discussion

The mean pesticide penetration through nonwoven fabrics is summarized in Table 18. An Analysis of Variance (ANOVA) showed that fabric ID was significant and accounted for the majority of the variability among difference (Table 21) in pesticide penetration through fabrics. Figure 24 illustrates the inferior performance of Duraguard® with all three pesticides. Duncan's multiple range test was applied to the means to isolate the difference. Tables 19, 20, and 21 and Figures 25, 26, and 27 show the groupings according to pesticide. Group 1 fabrics allowed the greatest penetration with all 5 replications in the study. Duraguard®, a 100% polypropylene nonwoven fabric, allowed the greatest penetration for all three pesticides. This nonwoven fabric has been tested in field studies and was considered to be more comfortable than Tyvek®. The results of this laboratory screening show that Duraguard® would not be an alternative to nonwoven fabrics such as Tyvek® as it allows pesticide penetration and would not serve as a fully protective barrier.

A second group of fabrics (Group 2, Table 19, 20 and 21) was more protective than Group 1, but at least two or more samples allowed pesticide penetration. This group of fabrics also had replication in which at least one or more had zero penetration. These findings could indicate a lack of uniformity in the quality control of nonwoven fabrics. Previous evaluation showed that Tyvek®

Table 17. FABRIC DESCRIPTIONS: NONWOVEN STUDY

Code	Common Name	Fiber Content	Construction	Finish
N1	Tyvek®	100% Polypropylene	Nonwoven	UF^{+}
N2	Tyvek®	100% Polypropylene	Nonwoven	F++
N3	Sontara	Polyester/Wood Pulp	Nonwoven	UF
N4	Sontara	Polyester/Wood Pulp	Nonwoven	F
N7	SMS	100% Polypropylene	Nonwoven	UF
N15	UT Ex.*	100% Polypropylene	Nonwoven	UF
N16A	UT Ex.*	100% Polypropylene	Nonwoven	F^{1}
N16B	UT Ex*	100% Polypropylene	Nonwoven	F^{2}
N17	Duraguard®	100% Polypropylene	Nonwoven	UF
N18	Duraguard®	100% Polypropylene	Nonwoven	F
W23	Chambray	100% Cotton	Plain Weave	UF
W25	Denim	100% Cotton	Twill Weave	UF

+UF - Unfinished
$^{++}$F - Fluorocarbon
$^{+++}$F1 - One sides fluorocarbon
$^{++++}$F2-Both sides fluorocarbon
* - Experimental

Table 18. PESTICIDE PENETRATION THROUGH NONWOVEN FABRICS

		Pesticide Penetration µg/cm^{2}					
Code	Fabric	Chlorobenzilate	SD	Dicofol	SD	Ethion	SD
N1	Tyvek®	(5) ND	.000	(5) ND	.000	(5) ND	.000
N2	Tyvek®	(5) ND	.000	(5) ND	.000	(5) ND	.000
N3	Sontara	(5) ND	.000	(5) ND	.000	(5) .011	.010
N4	Sontara	(5) ND	.000	(5) .009	.020	(5) .019	.042
N7	SMS	(5) ND	.000	(5) ND	.000	(5) ND	.000
N15	UT Ex*	(5) ND	.000	(5) ND	.000	(5) ND	.000
N16A	UT Ex*	(5) ND	.000	(5) ND	.000	(5) ND	.000
N16B	UT Ex*	(5) ND	.000	(5) ND	.000	(5) .008	.017
N17	Duraguard®	(5) .208	.132	(5) .068	.019	(5) .121	.076
N18	Duraguard®	(5) .174	.039	(5) .076	.025	(5) .074	.141
W23	Chambray	(5) .059	.040	(5) ND	.000	(5) .043	.008
W25	Denim	(5) ND	.000	(5) ND	.000	(5) ND	.000

ND -- non detectable
(#) -- number of replications SD -- standard deviation

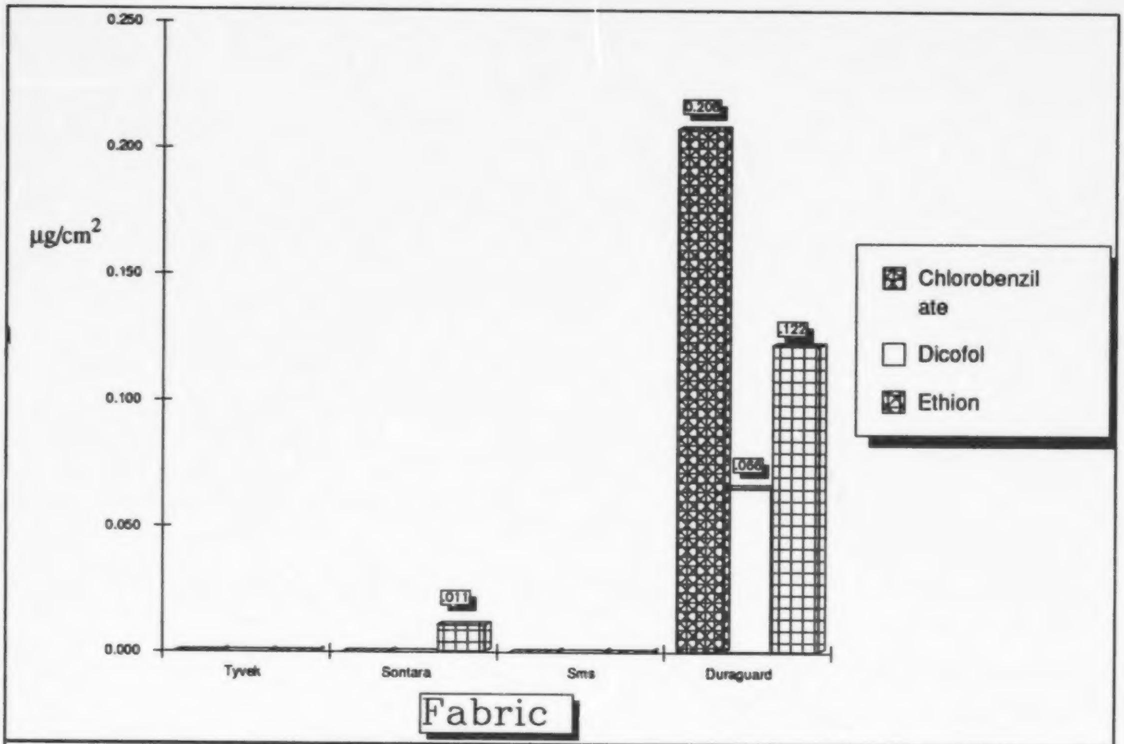


Figure 24. Pesticide Penetration through Nonwoven Fabric

Table 19. DUNCAN'S MULTIPLE RANGE TEST - CHLOROBENZILATE

	Groupings	Mean (μg/cm^2)	Code	Common Name	
	A	.208	N17	Duraguard®	F*
Group 1	A	.174	N18	Duraguard®	F
	B	.059	W23	Chambray	UF**
	C	ND	N15	UT Ex	UF
	C	ND	N16A	UT Ex	F
	C	ND	N16B	UT Ex	F
Group 3	C	ND	N2	Tyvek®	F
	C	ND	N3	Sontara	UF
	C	ND	N7	SMS	UF
	C	ND	W25	Denim	UF
	C	ND	N1	Tyvek®	UF
	C	ND	N4	Sontara	F

ND non detectable *F-Finished **UF-Unfinished

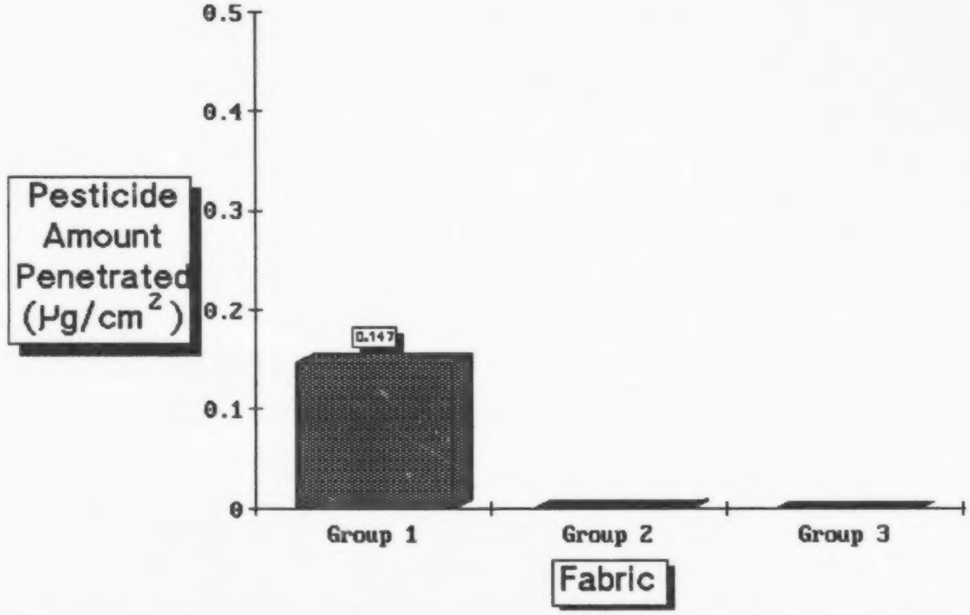


Figure 25. Duncan's Multiple Range Test - Chlorobenzilate

Table 20. DUNCAN'S MULTIPLE RANGE TEST - DICOFOL

	Groupings	Mean ($\mu g/cm^2$)	Code	Common Name	
Group 1	A	.076	N18	Duraguard®	F
	A	.068	N17	Duraguard®	UF
Group 2	B	.009	N4	Sontara	F
	C	ND	N15	UT Ex	UF
	C	ND	N16A	UT Ex	F
	C	ND	N16B	UT Ex	F
Group 3	C	ND	N2	Tyvek®	F
	C	ND	W23	Chambray	UF
	C	ND	N3	Sontara	UF
	C	ND	N7	SMS	UF
	C	ND	W25	Denim	UF
	C	ND	N1	Tyvek®	UF

ND non detectable *F-Finished **UF-Unfinished

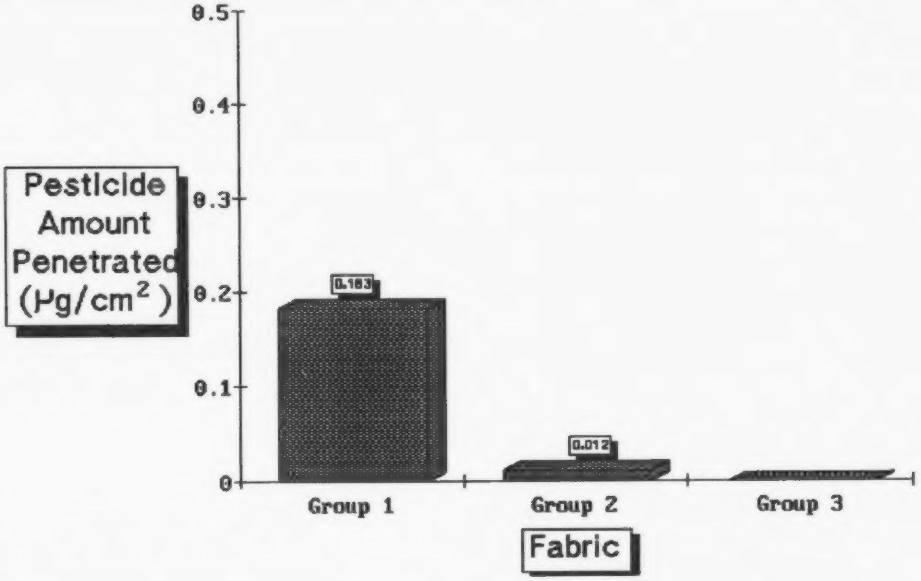


Figure 26. Duncan's Multiple Range Test - Dicofol

Table 21. DUNCAN'S MULTIPLE RANGE TEST - ETHION

	Groupings	Mean (µg/cm^2)	Code	Common Name	
Group 1	A	.121	N17	Duraguard®	UF
	B	.074	N18	Duraguard®	F
	B	.043	W23	Chambray	UF
Group 2	C	.019	N4	Sontara	F
	C	.011	N3	Sontara	UF
	C	.008	N16B	UT Ex	F
	D	ND	N15	UT Ex	UF
Group 3	D	ND	N16A	UT Ex	F
	D	ND	N2	Tyvek®	F
	D	ND	N7	SMS	UF
	D	ND	W25	Denim	UF
	D	ND	N1	Tyvek®	UF

ND non detectable

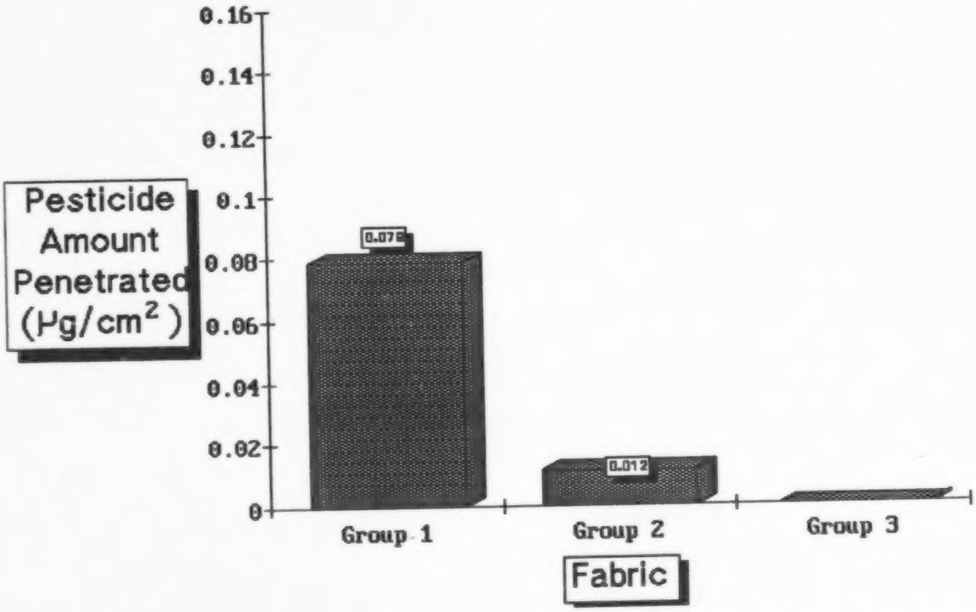


Figure 27. Duncan's Multiple Range Test - Ethion

had variable results when tested for penetration. These results were attributed to the lack of uniformity in the structure of Tyvek®, i.e. to the thick and thin sectors visually noted in the fabric construction. The results of this study indicate similar results; however, additional testing is recommended to test the uniformity of nonwoven fabric structures.

As noted in Tables 19, 20, and 21, a larger grouping of nonwoven fabrics (Group 3) provided excellent protection from pesticide penetration. All 5 replications proved to fall within the nondectable range. Therefore, these fabrics have proved to provide the greatest protection from pesticide penetration.

Conclusion

Nonwoven fabrics offer protection from pesticide spray penetration. Uncoated Tyvek® was shown to provide barrier qualities for all three pesticides used in this study. However, alternative fabrics, such as SMS, unfinished Sontara, and two of the experimental fabrics at The University of Tennessee, Knoxville, offer equal protection.

EFFECTS OF EXTERNAL PRESSURE AND CONTAMINATION LEVEL ON PESTICIDE PENETRATION OF FABRICS

In laboratory spray studies to this point, fabrics are held fixed in a horizontal plane perpendicular to the spray nozzle. That is, the fabrics are "passive," without stress or movement during the contamination procedure. In field conditions, worker motions, such as bending, stretching or leaning against solid objects, may result in fabric stresses that could affect pesticide penetration. Such effects should be evaluated if possible in laboratory spray testing.

It must also be noted that in previous laboratory spray testing, all fabrics were subjected to a uniform pesticide contamination level that was equivalent to an average worker's hourly pesticide exposure. In field testing, exposure levels greater than this average level must also occur. Therefore a rigorous laboratory test should attempt to estimate the protection level of a fabric in this worst case in addition to the average case. That is, it is probable that a fabric's protection level would vary as the contamination level is increased to the saturation or breakthrough level for the fabric.

Minor et al. (13) reviewed and tested the mechanisms of liquid penetration of textiles. Their study showed that there were four major mechanisms of liquid penetration of textiles:

1. Capillary penetration was defined as penetration that was promoted primarily by capillary forces.

2. Pressure penetration was defined as penetration that was promoted primarily by an external mechanical force.

3. Impact penetration was defined as penetration that was due primarily to the momentum of the liquid as it was thrown against the outside of the fabric.

4. Evaporation-Condensation was defined as penetration that was caused by the evaporation of a volatile liquid followed by condensation against the skin.

Minor et al. (13) showed that most fabrics of high cover have high impact penetration resistance. They also found that the application of an external pressure on a fabric greatly reduced the liquid breakthrough threshold of the fabric. That is, the fabrics under pressure as low as one psi had much less capacity to store the liquid internally.

The effect of repellent finish was shown to be counterproductive when testing the pressure penetration resistance of fabrics. The explanation for this effect was that the repellent finish sealed off the internal fiber structure, which reduced the ability of the fibers to store the test liquid. When pressure was applied, the liquid was forced to pass between the fibers and, therefore, through the fabric (13). Thus it was determined that the effects of increased pesticide contamination levels and the application of external pressure should be investigated.

Preliminary Study

The purpose of the preliminary study was to explore the effects of external pressure on pesticide penetration through fabrics.

The second purpose was to determine whether seams provided more or less protection.

Experimental Design--

Modifications of Standard Spray Test--The standard spray test method (see Appendix A) was used with the following modifications. The pesticide spray mix contained a dye. The test assembly contained a collector layer that was a sheet of white paper. An external pressure was applied to certain samples immediately following contamination. In the preliminary study the penetration was evaluated qualitatively by the visual inspection according to the method of Minor et al. (13).

Fabrics--Two plain woven cotton fabrics, light-weight poplin, medium-weight broadcloth, were acquired from Testfabrics Inc., Hoboken, New Jersey. Fabric descriptions and characteristics are given in Table 22.

Table 22. FABRIC DESCRIPTIONS: PRELIMINARY PRESSURE STUDY

Common Name:	Broadcloth	Poplin
Fabric Code:	W1	W3
Fiber Content:	Cotton	Cotton
Fabric Construction:	Plain Weave	Plain Weave
Finish:	None	None
Weight (g/m^2)	250.3	121.0
Yarn Count:	112 x 54	142 x 63
Air Permeability (m^3/sec-m^2):	.03	.22
Spray rating:	0	0
Mean Dicofol Penetration (μg/cm^2):	.004	.049

Weight - ASTM D3776-79
Yarn Count - ASTM D3775-79
Air Permeability - ASTM D3737-75
Spray Rating - AATCC 22-1980
*from weight and thickness study

The standard fabric assembly (see Appendix A) was modified by using a sheet of high-quality white bond paper as the collector layer rather than a cotton/polyester knit fabric.

Fabric samples were evaluated flat, and for exploratory purposes one half of the fabric samples were seamed in the center of the test specimens. The stitching density was 15.24 to 20.32 stitches per cm.

Pesticide--The pesticide Dicofol was used in a 0.12% solution. A dye, Basic Blue 41 (Maxilon Blue GRLA), was added to the spray solution to yield a 1% dye solution. Microscopic evaluation revealed that the pesticide dye solution was stable. The wicking behavior of the pesticide/dye solution was compared with that of the pesticide solution. The ends of two vertical strips of cotton fabric, one inch wide, were immersed in both solutions, and the height of the wicking liquids were compared at one and five minutes. The wicking behavior of the pesticide solution was not significantly altered by the dye; and the dye remained in solution as the liquid penetrated the fabrics and did not concentrate on the fibers. Thus the penetration of the dye was an adequate qualitative indicator of pesticide penetration.

Application of pressure--All specimens were contaminated by a single pass. Two replications were evaluated for each fabric test. After contamination one half of the specimens were removed from the spray chamber and dried for one hour.

An external pressure (nominal value 1 psi) was applied to the other fabrics in the following manner. A square glass plate (4" by 4") was placed on the center of a contaminated fabric within 15 seconds after contamination. A sixteen pound weight was immediately placed on the center of the glass plate. In one test the weight was left on the test fabric for one hour. In a second test the time was 24 hours before weight removal. After removal of the weight, the fabrics were dried for one hour.

Visual evaluation--After the test assembly was dried, the penetration of the pesticide/dye solution was tentatively evaluated by visual inspection of the white bond paper collector layer. The appearance of the dyed test fabric was also inspected. This allowed for rapid but qualitative evaluation of pesticide penetration for an estimate of fabric saturation by the comparison of depth of color on the fabric face and back. The fabrics were ranked by examining the collector paper layers according to the extent of staining: negligible, light, moderate or heavy.

Results and Discussion--

Effect of Time--There was no observable difference between the one hour and the twenty-four hour tests. This indicated that one hour of pressure on the fabric was sufficient to allow equilibrium penetration.

Effect of Pressure--The penetration results are shown in Table 23. Without applied pressure the penetration through the medium-weight fabric was negligible. Comparison of the face and the back of the test fabric revealed that the medium-weight fabric was not saturated. That is, the dye had not uniformly penetrated the fabric; the face of the fabric was much darker than the back of the fabric.

Table 23. PESTICIDE PENETRATION: PRELIMINARY PRESSURE STUDY

Condition	Poplin (lt.wt.)	Broadcloth (med.wt.)
Control (w/o pressure, w/o seam)	Moderate	Negligible
Seam (w/o pressure)	Light (less at seam)	Negligible
Pressure (w/o seam)	Heavy	Heavy
Pressure/seam	Heavy (more at seam)	Heavy (less at seam)

* w/o=without

The pesticide/dye penetration of the light-weight fabric was apparent by the moderate degree of staining of the collector paper. Comparison of the face and back of the light-weight fabric showed that the light-weight fabric was saturated.

When pressure was applied to the medium-weight fabric, the penetration to the collector layer was evaluated as heavy. When the fabric was compressed by the external pressure, the uniform distribution of dye in the fabric indicated that the fabric was saturated.

When pressure was applied to the light-weight fabric the penetration to the collector layer was heavy. The light-weight fabric was saturated with or without pressure.

Without pressure the seam section of the fabric appeared to have less penetration. In the seamed section, for the medium weight fabric the collector paper was essentially unstained. In the case of the light-weight fabric the collector layer revealed less penetration at the seam.

When pressure was added, light weight fabric with a seam revealed greater penetration in the seam area. The seam in this case may have functioned as a channel for the flow of pesticide solution. For the medium-weight fabric with a seam and under pressure, the collector layer showed there was decreased penetration at the seam.

Preliminary Conclusions--

The following conclusions were drawn from the preliminary research:

1. External pressure increased penetration.
2. The effect of fabric saturation needs further investigation.

3. Seams may have the potential to increase or decrease penetration.

Pressure Study

The preliminary study led to the investigation of application of external pressure and increased severity of the standard spray solution. From the research of Minor, et al (13), it is known that pressure may also change the relative rankings of fabrics as well as increase the total penetration levels. Thus pressure tests as well as pure wicking tests (no pressure) would need to be conducted at varying levels of pesticide contamination to fully characterize fabrics in the laboratory.

Fabrics--

Four nonwoven fabrics (Table 24) were selected for evaluation.

Table 24. FABRIC CHARACTERISTICS: PRESSURE STUDY

Fiber Content	Sontara Wood Pulp/ Polyester		SMS Polypropylene	
Fabric Construction	Spunlace		Melt blown/Spunbond/ Melt blown	
Repellent Finish(Code)	UF(N3)	F(N4)	UF(N9)	F(N10)
Weight($\mu g/m^2$)	71.5	72.7	60.5	62.4
Air Permeability ($m^3/sec/m^2$)	0.267	0.298	0.090	0.056
Spray Rating (0-100)	0	90	90	70
Surface Energy (Oil Repellency Rating Number)	0	8	0	8

UF unfinished
+F finished

Weight - ASTM D3776-79
Air Permeability - ASTM D3737-75
Spray Rating - AATCC 22-1980
Surface Energy Rating - AATCC 118-1983

Pesticides--

Two pesticides were investigated: Dicofol and Terrazole® in a 0.12% solution.

Exposure--

The spray chamber was used to contaminate the fabric samples. The fabric assemblies were subjected to one, two, or three passes of the spray solution. One set of fabrics was sprayed, dried, and extracted without application of external pressure. The second set of fabrics was sprayed, and within 15 seconds after contamination, a weight was placed on the test fabric. The weight was 16 pounds and it was placed on a 4" square glass plate located at the center of the test assembly. Thus the nominal pressure level was one psi. The weight was removed after one hour and the assembly was dried for one hour before the fabric layers were extracted and analyzed (see Appendix A).

Results and Discussion--

Dicofol: Effect of Pressure--Dicofol penetration results are summarized in Tables 25 and 26. At the highest level of contamination, (three passes) unfinished Sontara had the greatest pesticide penetration. However, even in this case, the fabric prevented more than 96% of the pesticide from passing to the collector layer. At the lowest contamination level (one pass) unfinished "SMS" prevented more than 98% Dicofol penetration. In all other cases of Dicofol penetration, pesticide barrier levels were greater than 99%.

Table 25. CAPILLARY PENETRATION - DICOFOL

Fabric	Penetration (μg/cm^2)	SD** (μg/cm^2)	Penetration (% of Total) Contamination)
One Pass			
Sontara(Unfinished)	(1)*.031		.52
Sontara(Finished)	.020		.34
SMS(Unfinished)	(2) .090	.016	1.52
SMS(Finished)	(1) .022		.37
Two Passes			
Sontara(Unfinished)	(3) .085	.098	.53
Sontara(Finished)	(2) .024	.006	.15
SMS(Unfinished)	(1) .022		.14
SMS(Finished)	(2) .026	.009	.16
Three Passes			
Sontara(Unfinished)	(5) .736	.577	3.53
Sontara(Finished)	(5) .049	.013)	.24
SMS(Unfinished)	(4) .069	.021	.33
SMS(Finished)	(5) .062	.011	.30

(*) Number of replications included in analysis.
** SD=Standard Deviation

Table 26. PRESSURE PENETRATION - DICOFOL

Fabric	Penetration (μg/cm^2)	SD** (μg/cm^2)	Penetration (% of Total Contamination)
One Pass			
Sontara(Unfinished)	(4)*.216	.051	3.19
Sontara(Finished)	(5) 1.474	.176	21.74
SMS(Unfinished)	(1) .023		0.34
SMS(Finished)	(2) 1.274	.011	18.78
Two Passes			
Sontara(Unfinished)	(4) .670	.667	5.15
Sontara(Finished)	(5) 4.114	1.587	31.57
SMS(Unfinished)	(5) .654	1.047	5.02
SMS(Finished)	(5) 3.350	.859	25.71
Three Passes			
Sontara(Unfinished)	(4) 3.150	1.084	18.43
Sontara(Finished)	(4) 6.925	2.814	40.52
SMS(Unfinished)	(5) 5.283	3.066	30.91
SMS(Finished)	(5) 4.432	2.073	25.93

(*) Number of replications included in analysis.
** SD= Standard Deviation.

By comparison, the Dicofol penetration with added pressure (Table 26) shows greater penetration occurred. In most cases, the pesticide penetration with pressure was one or two orders of magnitude greater. The barrier level ranged from 99+% to as low as 60%.

Table 27 summarizes the analysis of variance test for Dicofol penetration. The significant factors were pressure and contamination level (number of passes). The significant interaction between pressure and fabric and the relatively low significance of the fabric variable in the overall analysis (Table 27) indicated that it would be advantageous for the purpose of analysis to analyze separately the pressure and contamination level results.

Table 27. ANALYSIS OF VARIANCE: DICOFOL PENETRATION

Source	DF	Sum of Squares	Mean Square	F Value	PrF
Fabric	3	12.6608	4.2203	2.82	.04310
No. Pass	2	37.7408	18.8704	12.60	1.E-05
No. Pass x Fabric	6	13.4950	2.2492	1.50	.18566
Pressure	1	104.9718	104.9718	70.11	5.E-13
Pressure x Fabric	3	23.1636	7.7212	5.16	.00239
No. Pass x Pressure	2	4.8829	2.4411	1.63	.20124

Contamination Level Penetration of Dicofol--Table 28 summarizes the analysis of variance data for Dicofol capillary penetration. The only significant factor was the level of contamination (number of passes). Fabric was not a significant factor in evaluating the effect of the level of contamination on penetration.

Table 28. ANALYSIS OF VARIANCE:DICOFOL CONTAMINATION LEVEL

Source	DF	Sum of Squares	Mean Square	F Value	Pr F
Fabric	3	2.7097	0.9032	0.62	.60321
No. Pass	2	12.3765	6.1882	4.27	.01919
No. Pass x Fabric	6	5.4234	1.0847	0.75	.59099

Pressure Penetration of Dicofol--In the case of pressure penetration of Dicofol, the analysis of variance (Table 29) showed that fabric was a very significant factor. This result is in strong contrast to that obtained for level of contamination of Dicofol. As noted in Table 26, there were large differences in mean penetration values between fabrics. The fabric-contamination interaction factor was significant in the pressure tests. The data in Table 26 show that at the highest contamination level all of the fabrics performed poorly. At this level, under pressure, all of the fabrics were saturated by the volume of the pesticide spray. That is, the inherent differences between the fabrics were overwhelmed by the effect of contamination level when the contamination level was at the highest level.

Table 29. ANALYSIS OF VARIANCE: DICOFOL PRESSURE

Source	DF	Sum of Squares	Mean Square	F Value	Pr F
Fabric	3	38.2637	12.7546	10.94	2.E-05
No. Pass	2	38.9493	19.4746	16.70	6.E-06
No. Pass x Fabric	6	30.9739	5.1623	4.43	.00166

Duncan's multiple range test was performed on the fabric variable in the case of pressure penetration (Table 30). This test resulted in the separation of the four fabrics into two distinct groups. The two repellent finished fabrics were in the group of highest Dicofol pressure penetration. This analysis infers that repellency finishes may be counterproductive to the pressure penetration resistance of fabrics.

Table 30. DUNCAN'S MULTIPLE RANGE TEST: PRESSURE STUDY

Fabric	Mean Penetration ($\mu g/cm^2$)	Duncan Grouping
SMS(Finished)	3.049	A
Sontara(Finished)	2.442	A
Sontara(Unfinished)	.6194	B
SMS(Unfinished)	.4725	B

Terrazole®-- Terrazole® penetration results are summarized in Tables 31 and 32. Table 33 summarizes the analysis of variance data for the penetration of Terrazole®. The significant factors in the penetration of Terrazole® were pressure and contamination level. Fabric was not a significant factor. These results sharply contrast the penetration results for Dicofol. Also the penetration level of Terrazole® was high in the penetration tests, whereas testing of dicofol in

Table 31. TERRAZOLE® PENETRATION

Fabric	Penetration ($\mu g/cm^2$)	SD** ($\mu g/cm^2$)
One Pass		
Sontara(Unfinished)	(3)*.047	.028
Sontara(Finished)	(5).101	.070
SMS(Unfinished)	(5).113	.070
SMS(Finished)	(5).150	.1389
Two Passes		
Sontara(Unfinished)	(5).339	.190
Sontara(Finished)	(5).239	.162
SMS(Unfinished)	(5).277	.170
SMS(Finished)	(5).444	.295

(*) Number of replications included in data.

**SD = Standard Deviation.

Table 32. TERRAZOLE® PRESSURE PENETRATION STUDY

Fabric	Penetrtion ($\mu g/cm^2$)	SD** ($\mu g/cm^2$)
One Pass		
Sontara(Unfinished)	(5)*.730	.428
Sontara(Finished)	(5).581	.246
SMS(Unfinished)	(3).535	.440
SMS(Finished)	(4).838	.337
Two Passes		
Sontara(Unfinished)	(5)1.658	1.282
Sontara(Finished)	(5)1.409	.994
SMS(Unfinished)	(5).940	.485
SMS(Finished)	(5)1.028	.611

(*) Number of replications included in data.

*SD = Standard Deviation.

Table 33. ANALYSIS OF VARIANCE TERRAZOLE® PENETRATION

Source	DF	Sum of Squares	Mean Square	F Value	Pr F
Fabric	3	1.6965	0.5655	0.80	.49884
No. Pass	1	14.4886	14.4886	20.48	3.E-05
No. Pass x Fabric	3	0.6906	0.2302	0.33	.80692
Pressure	1	46.3326	46.3326	65.51	3.E-11
Pressure x Fabric	3	1.6892	0.5631	0.80	.50071
No. Pass x Pressure	1	1.8552	1.8552	2.62	.11040

similar experiments usually resulted in non-detectable penetration. Terrazole® penetrated fabrics to an extent greater than Dicofol.

Conclusions--

Application of external pressure and contamination at higher levels have been shown to increase pesticide penetration through fabrics during laboratory testing (see Table 71 in Appendix C). In particular, research has shown that application of pressure may change the relative rank or grouping of fabrics evaluated in laboratory tests. External pressure was shown to cause increase penetration by one or two orders of magnitude. Such pressure could easily occur when a worker leans against the tractor cab or rests his arm upon his leg.

Clearly, in the engineering and evaluation of fabrics for protective apparel, the fabric's resistance to penetration by pressure should be taken into consideration. In laboratory testing this has been shown to represent a worst case.

Research has also shown that in the case of pressure penetration repellency treatments may be counter-productive. These finishes may seal off the fibers as a reservoir to store pesticide. When pressure is applied to the fabric and the pesticide solution on the fabric, the pesticide must either pass into the fibers or pass through the fabric. It is by no means suggested that repellant finishes are not vital for the protection of spray applicators. The use of such finishes may allow protective garments to be constructed from natural fibers that are more comfortable to the wearer and are often more acceptable to the consumer. What is suggested is that the role of absorbency and internal fiber storage of pesticide as well as fabric surface energy must be considered in the manufacturing of the next generation of protective clothing for pesticide spray applicators.

EFFECT OF SEAMS AND CLOSURES ON PESTICIDE PENETRATION

Researchers have identified the parts of the body that are exposed to the highest level of pesticide: the forearm, shoulder, and the thigh. Maibach et al (14) applied pesticides labeled with radioactive carbon directly to the skin to study the areas of the body affected by pesticide deposits. The results showed that the underarm absorbed 64% of the pesticide applied, the upper forearm 29%, and the scrotum 100%. These results demonstrate the need for providing a barrier between the skin and the pesticide. Clothing may be specially designed to provide the extra protection needed for these high pesticide depositions, and high absorption areas of the skin.

In the study reported by Staiff et al. (17) the researchers evaluated semi-disposable jackets or jacket and trouser for use during spraying at very high temperatures. The results showed the garments provided protection, however, some leaked around the seams. As the shoulder seams became stretched (one of the areas of high pesticide deposition), they allowed leakage either through the seam or through the elongated stitch openings. Staiff et al. (7) recommended additional work for evaluating and developing seams. The purpose of this study was to evaluate seams and closures and to indentify those which best provides a barrier to pesticides.

Preliminary Market Survey

Initially a market survey was used to identify the types of protective apparel available in today's market. Contacts were made with companies identified in the Thomas Register as manufacturers of protective apparel. Thirty companies responded by sending information on their line of protective apparel. Garments were secured from these companies and examined to identify the types of seams, zippers, and closures. Both metal and nylon zippers were used. The seams were overlock stitch 504 and the plain stitch 301 as determined by Federal Standard 751a. The thread used in the seam construction was a synthetic 100% polyester, and the number of stitches averaged .254 per cm.

Experimental Design

The variations of seams, zippers and fabrics used to evaluate their effect on pesticide penetration are described in Table 34.

Table 34. SEAMS AND ZIPPERS DESCRIPTION

Dicofol - Seams

Fabrics	Seams
Denim	Plain
Tyvek®	Flatfell
SMS	Bound
Sontara	Overlock Inside Seam
	Overlock Outside Seam
	No Seam

Terrazole - Seams

Fabrics	Seams
Denim	Plain
Tyvek®	Overlock Inside Seam
	Overlock Outside Seam
	No Seam

Dicofol - Zipper

Fabrics	Zipper Closures
Tyvek®	Centered
	Lapped Traditional
	Lapped Experimental
	Open Face Nylon

Fabrics

Fabrics were selected because they had been shown to provide resistance to pesticide penetration as determined in previous studies. Table 35 and 36 identifies fabric descriptions and performance characteristics.

Table 35. FABRIC DESCRIPTIONS: SEAMS AND ZIPPERS STUDY

Code	Common Name	Fiber Content	Construction	Finish
W25	Denim	100% Cotton	Woven-twill	None
N1	Tyvek®	100% Polypropylene	Nonwoven-PB	None
N4	Sontara	Polyester/Wood Pulp	Nonwoven	FL
N8	SMS	100% Polypropylene	Nonwoven-SB/MB/SB	FL

PB - Point bonded
SB - Spun bonded
MB - Melt blown
FL - Fluorocarbon water repellent

Table 36. FABRIC CHARACTERISTICS: SEAMS AND ZIPPERS STUDY

Fabric	Thickness (mm)	Weight (g/m^2)	Air Permeability (m^3/sec/m^2)	Spray Rating	Yarn warp	Count fill
Denim	0.66	276.3	0.13	0	71	49
Tyvek®	0.10	45.6	0.009	90	NA	NA
Sontara	0.32	72.7	0.298	90	NA	NA
SMS	0.29	62.4	0.056	70	NA	NA

The following methods were used:
Thickness - ASTM D177-64
Weight - ASTM D3776-79
Air Permeability - ASTM D3737-75
Spray Rating - AATCC 22-1980
Yarn Count - ASTM D3775-79

Sample Preparation

Samples, seams and closures were prepared using standard operating procedures (see Appendix A).

Pesticide

Dicofol and Terrazole® were used in this study at a 0.12% solution. The fabric samples were contaminated according to standard procedures (see Appendix A). For the pesticide Terrazole®, the fabric samples were exposed to two sprayings. The intent was to provide a more aggressive spray.

Extraction and Analysis

The extracts were prepared according to standard procedure (see Appendix A) and analyzed by high performance liquid chromatography (HPLC), using a Waters number 600E multisolvent delivery system.

Results and Discussion

Dicofol: Seams--

Four fabrics without seams were examined to provide the base line for evaluating the effect of seams on pesticide penetration. The results showed that for only one fabric (SMS) did a seam allow penetration.

Of the seams evaluated, 14 of 20, allowed penetration.Table 37 shows the results of the amount of pesticide that penetrated for each of these 14 seams. The percentage of seam samples that allowed pesticide penetration are shown in Table 38. For example, 40%, two out of the five Sontara overlock inside seam samples, allowed penetration of the pesticide. Duncan's multiple range test was performed on rankings. This nonparametric analytical procedure was selected due to the heterogeneity of subgroups. The analysis showed no significant differences among the seams (Table 39. The limited size of the sample prevented discrimination among seams. Therefore, the conclusion was there are no significant differences between seams. Therefore a second pesticide was selected to further evaluate the effect of seams.

Table 37. DICOFOL PENETRATION: SEAM STUDY

Fabric/Seam Description	Amount Penetrate ($\mu g/cm^2$)	Standard Deviation
Tyvek®ovr/in*	0.109	0.153
Tyvek® ovr/out**	0.059	0.000
SMS flatfell	0.037	0.027
Sontara flatfell	0.026	0.0
Tyvek® plain	0.026	0.0
Tyvek® flatfell	0.025	0.0
Denim bound	0.023	0.005
SMS bound	0.016	0.0
Denim ovr/out	0.013	0.0
Sontara ovr/out	0.013	0.0
Tyvek® bound	0.013	0.0
Sontara ovr/out	0.013	0.0
SMS plain	0.010	0.004
Sontara plain	0.001	0.0

*One/in overlock inside.

**One/out overlock outside.

Table 38. MEAN PERCENTAGE OF SEAMS FOR DICOFOL

Fabric/Seam Description	Percentage Penetration %
Denim Bound	0.40
Denim ovr/out	0.25
Tyvek® plain	0.20
Tyvek® flatfell	0.17
Tyvek® bound	0.20
Tyvek® ovr/out	0.20
Tyvek® ovr/in	0.60
SMS plain	0.60
SMS flatfell	0.40
SMS bound	0.20
SMS no seam	0.20
Sontara plain	0.20
Sontara flatfell	0.20
Sontara ovr/out	0.20
Sontara ovr/in	0.40

Table 39. ANALYSIS OF VARIANCE FOR DICOFOL SEAM STUDY

Source	df	SS	MS	F	Level of Significance
SEAM	14	247.1792	176.128	0.52	0.9098

Terrazole®: Seams--

The mean penetration for the samples is shown in Table 40. Terrazole® penetrated both the denim and Tyvek® samples, with or without a seam construction; furthermore, the pesticide penetrated all five of the replications of each fabric type.

The differences among means were then partitioned through an orthogonal contrast analysis. The orthogonal design allows for the collection of observations that permit the estimation and testing of the various treatment effects and interaction effects separately (15). The two requirements that are necessary for an experiment to be regarded as a orthogonal design are as follows: (1) the observations within a treatment combination are sampled at random; (2) observations in each possible combination of treatments are the same (15). The usual procedure is to set up an experiment to be analyzed by two-way analysis or higher, as in this experiment, and to assign subjects at random and independently so as to have an equal number in each combination. This experiment followed the same procedure. Tables 40-42 illustrate these means, level of significance, and orthogonal contrast analysis. As in the previous study, the first step was to examine the difference between the no seam samples and the seams. The denim no seam had more penetration of the pesticide than the seams. This was verified with a 0.0013 level of significance (Table 42). However Tyvek® did not have a significant level of difference. The estimated difference for the Tyvek® no seam was a -0.100, which indicated the no seam had the higher level of penetration. The reason for the nonsignificant level is witnessed in the overlock outside seam which was the only seam construction which had a higher level of penetration than the no seam for the Tyvek® samples.

Table 40. TERRAZOLE® PENETRATION: SEAM STUDY

Fabric/Seam Description	Amt Penetrated ($\mu g/cm^2$)	Standard Deviation
Denim plain	0.485	.1956
Denim ovr/out	0.938	.2618
Denim ovr/in	1.044	.2236
Denim no seam	1.253	.3579
Tyvek® plain	0.388	.2148
Tyvek® ovr/in	0.709	.3194
Tyvek® ovr/out	0.797	.1325
Tyvek® no seam	0.732	.2667

Table 41. ANALYSIS OF VARIANCE TERRAZOLE® SEAM STUDY

Source	df	MS	F	Significance Level
TOTAL	42			
SEAM	7	0.4706	7.16	0.0001
ERROR	35	0.0657		

Table 42. ORTHOGONAL CONTRAST ANALYSIS OF SEAMS EXPOSED TO TERRAZOLE ®

Fabric	Denim	. Tyvek®									
Seams	Plain	In	Out	No	Plain	In	Out	No	Est.	Level	
	Means	0.485	0.938	1.044	1.253	0.388	0.709	0.797	0.732	Diff.	Sign.
No.	Contrast										
1	Denim vs Tyvek®	1/4	1/4	1/4	1/4	-1/4	-1/4	-1/4	-1/4	0.273	0.0013
2	No Seam vs Seam (Denim)	1/3	1/3	1/3	-1	0	0	0	0	-0.431	0.0013
3	No Seam vs Seam (Tyvek®)	0	0	0	0	1/3	1/3	1/3	-1	-0.100	0.4518
4	Plain vs Overlock (Denim)	1	-1/2	-1/2	0	0	0	0	0	-0.505	0.00005
5	Plain vs Overlock (Tyvek®)	0	0	0	0	1	-1/2	-1/2	0	-0.365	0.0092
6	In vs Out (Denim)	0	1	-1	0	0	0	0	0	0.106	0.5158
7	In vs Out (Tyvek®)	0	0	0	0	0	1	-1	0	-0.888	0.5924

The conclusion drawn from these comparisons is that denim with a seam construction provided a better barrier to the pesticide Terrazole® than did the denim no seam samples. The extra layers of fabric within the seam construction provide a barrier to the pesticide both physically and chemically. Denim's 100% cotton content gives it the physical property of being very hygroscopic, and thus would readily absorb the water content of the pesticide. However, the pesticide Terrazole® has no groups available to bond with the polar groups of the cellulose in denim.

Comparison was also made between the plain seam and the average of the overlock stitched seams inside and outside. In both the denim and the Tyvek® analyses the overlock seams allowed more penetration of the pesticide. The estimated difference for the denim was -0.505, and the level of significance was 0.0005. The estimated difference for the Tyvek® was -0.365, and the level of significance was 0.0092 (Table 42).

The final comparison made in the analysis was between the inside overlock stitch and the outside stitch. Although the estimated difference for both the denim and Tyvek® pointed to the overlock outside stitch as allowing more penetration, this result was not significant, as depicted in Table 42, with the level of significance being 0.5158 and 0.5924, respectively.

Dicofol: Zipper--

To evaluate zippers, Tyvek® was used in all zipper constructions to eliminate fabric effect. The pesticide used was Dicofol. Five different zipper constructions--a centered, a lapped traditional, a lapped experimental, an open face nylon, and an open-face metal construction were--evaluated. Sixteen replications of all zipper constructions were evaluated.

A comparison of the zippers with the no seam Tyvek® sample revealed the following: the no seam did not allow penetration of the pesticide. Twenty-two percent of the zipper samples allowed penetration.

Table 43 gives the percentage of the zipper samples for each zipper type which had penetration. For one percent of the centered zipper, which is most often used in agricultural protective garments, allowed penetration. That is, six out of the sixteen centered zipper replications allowed penetration of pesticide at 0.0002 level of significance (Table 44). Eight percent of the lapped traditional zippers allowed penetration; only one out of sixteen replications allowed penetration of the pesticide. From

Table 43. PERCENTAGE OF ZIPPERS WITH PENETRATION

Zipper Description	Percentage Penetrate %
Centered	41
Lapped Traditional	8
Lap Experimental	18
Open Nylon	24
Open Metal	16

the analysis of variance we can conclude that the lapped traditional zipper provided the best barrier to the pesticide Dicofol and that it was significantly different from the centered zipper, whose level of significance was 0.0307 (Table 45).

Table 44. ANALYSIS OF VARIANCE: DICOFOL ZIPPER STUDY

Zipper	LS Mean	STD Error	Significance Level LS Mean
Centered	0.4086	0.1026	0.0002
Lapped Traditional	0.0821	0.1049	0.4373
Lapped Experimental	0.1849	0.1024	0.0761
Open Nylon	0.2394	0.1025	0.0230
Open Metal	0.1555	0.1026	0.1351

Table 45. SIGNIFICANT LEVEL OF PROBABILITY BETWEEN ZIPPERS

Centered	Lapped Traditional	Lapped Experimental	Open Nylon	Open Metal
Centered	0.0307	0.1317	0.2496	0.0875
Lapped Traditional	0.0307	0.4877	0.2933	0.6206
Open Nylon	0.2496	0.2933	0.7111	0.5668
Open Metal	0.0875	0.6206	0.8414	0.5668

Note: Level of Significance = .05

Conclusions

The purpose of this study was to determine if seam and zipper constructions affected pesticide penetration. The results show that seams and zippers may alter the penetration of pesticides through fabrics for Dicofol, the seams and the zippers allowed penetration while the no seam constructions did not allow penetration. The best seam construction could not be isolated due to the sample size. In the evaluation of zippers, the lapped traditional zipper was shown to provide more protection than other zipper constructions. For Terrazole®, both the seam and no seam constructions allowed penetration, with the seams providing a better barrier to the pesticide. The plain seam provided the optimum barrier to the pesticide for both the denim fabric and the Tyvek® textile.

In the seam studies, denim allowed more Terrazole® to penetrate than Dicofol. This result could be attributed to the chemical differences of the pesticides and their interaction with the denim fiber content. Terrazole® has nothing to bond with the polar groups of the 100% cotton denim, whereas the Dicofol has an OH group which is available for bonding with the hydroxyl groups of the cotton.

Therefore, more Terrazole® will penetrate, since the denim will be unable to absorb the Terrazole® component of the pesticide emulsion.

Another conclusion from the Terrazole® seam study concerns the difference between the Tyvek® and denim fabrics. Tyvek® seam constructions allowed less penetration of the pesticide then the denim seam constructions as shown in Table 36. The level of significance was 0.0013. The reason for this difference is due to the fabric constructions. Denim is a tightly woven fabric which causes its yarns to act as wicks (16). Tyvek® is composed of fibers uniformly separated with discontinuous capillaries which are held in the fabric so that the surface tension of the liquid cannot pull them together. Thus capillary transport of the pesticide is avoided.

Seams and zipper constructions have been shown to alter the performance of pesticide penetration through fabrics. It is therefore recommended that seams and zippers type and placement be taken into consideration when developing protective clothing

PROFILE OF PESTICIDE PENETRATION

Various research studies have been concerned with the effect of textile structural parameters on the penetration of liquid through fabrics. Studies have shown that fiber content, fabric geometry, and finishes can influence the penetration of liquids through fabrics (2,8). In one study, the location of malathion in contaminated textiles composed of cotton or polyester was determined directly after staining with osmium and large deposits of malathion were observed on the yarn surfaces (17). In addition, the distribution of pesticide was uniform through polyester yarns, whereas cotton yarns contained more pesticides on their surface than in their yarn interiors. This study also found that cotton fibers exhibited a relatively constant pesticide concentration across the radius of individual fibers, although polyester fibers exhibited a higher concentration on their surface than their interior.

The primary purpose of this research was to obtain more information about the location of pesticides in fibers and fabrics. Rather than using osmium staining to locate pesticides indirectly, however, two other analytical techniques were employed that allowed us to directly determine the location of pesticide in the fibers and fabrics.

Fabrics and Pesticides

Three fabrics were evaluated: a 100% cotton twill, an identical 100% cotton twill treated with a fluorocarbon finish, and an experimental spunbonded-meltblown-spunbonded (SMS) polypropylene composite nonwoven fabric. The fluorocarbon finish applied to the cotton twill was a Corpel ^{TM} finish from DuPont. The two pesticides, Terrazole$^{®}$ and Dicofol were applied to the fabrics.

Exposure

Contamination of fabrics was achieved by two different methods: undiluted liquid pesticides were pipetted directly onto the fabric face, or a dilute pesticide solution was sprayed onto the fabric face using the spray chamber. Unlike conventional use of the spray chamber, however, a backing fabric was not placed under the contaminated fabric, and the fabric to be analyzed was subjected to a multiple spray sequence consisting of two sprays with a 0.12% pesticide solution, drying for one hour, two more sprays, another hour of drying, and then two more sprays for a total of six sprays. This spray sequence allowed more pesticide to accumulate on the fabric so that detection was more easily achieved without significantly increasing the typical wetness of sprayed fabrics.

Analysis

After contamination, fabric samples were desiccated and stored in a freezer at approximately -10°C until analysis. X-ray photoelectron spectroscopy (XPS) was performed on 1 cm x 1cm squares cut from near the center of each fabric after placing the square on a slightly larger square of aluminum foil and folding the foil around the edges of the fabric square to secure loose fibers.

A Perkin-Elmer 5100 x-ray photoelectron spectrometer with an aluminum K_2 source was used to collect all XPS spectra. Three photoelectron binding energy regions were examined in the multiplex spectra of Terrazole® contaminated fabrics. These corresponded to nitrogen 1s, carbon 1s, chlorine 1s and sulfur 1s photoelectrons. Since Terrazole® is composed of nitrogen, chlorine and sulfur atoms, atomic concentrations of these elements were used as a measure of Terrazole® concentration in contaminated fabrics. One photoelectron binding energy region was examined in the multiplex spectra of Dicofol-contaminated fabrics. This corresponded to chlorine 1s photoelectrons. The atomic concentration of chlorine was used as a measure of Dicofol concentration. Atomic concentrations were compouted from the multiplex spectra using standard instrument software (18). Since these elements also may be present in uncontaminated fabrics, their concentrations in contaminated fabrics were compared to those in uncontaminated fabrics.

In general, only atoms in the first 10-20 Angstroms of a sample surface contribute to XPS spectra so additional spectra were collected after atoms were sputtered off the surface of fabrics with argon ions to obtain information about pesticide penetration further into fibers. After an XPS spectrum was collected from an original contaminated fabric sample, it was sputtered with a 15 microampere argon ion gun for various times, and XPS spectra were collected again to provide atomic concentrations at various depths up to about 50-100 A below the original (unsputtered) sample surface.

Fourier transform infrared photoacoustic spectroscopy (FTIR/PAS) was performed using either a 0.5 cm x 0.5 cm square cut from near the center of each contaminated fabric after securing the fabric in aluminum foil similar to the samples prepared for XPS analysis or a powder made by grinding a contaminated fabric in a Wiley mill.

A Digilab FTS-40 equipped with a Digilab photoacoustic detector was used to collect FTIR/PAS spectra with a resolution of 8 cm^{-1}. After introducing a sample into the detector, it was purged with nitrogen gas for one hour to remove ambient gases from the sample. All spectra were referenced to spectra from carbon black collected with the same instrument settings. In FTIR/PAS, only heat from IR absorption that is generated within one thermal diffusion length of the sample surface can escape from the sample and contribute to signals in FTIR/PAS spectra. Thermal diffusion lengths of cotton and polypropylene were computed using standard techniques (19) and are presented in Table 46 for different interferometer optical velocities.

The FTIR/PAS data provided information from deeper within samples than XPS. Since cotton fiber diameters were in the 14-17 micrometer range and SMS fiber diameters were in the 15-20

Table 46. THERMAL DIFFUSION LENGTHS COMPUTED FOR COTTON
1000 CM^{-1}

Optical Velocity (cm/s)	Thermal Diffusion Length (micrometer) cotton	SMS
0.158	9.8	12.8
0.317	6.9	9.1
0.633	4.9	6.4

micrometer range, analysis depths for an absorption band in the 1000 cm^{-1} spectral region included about 2/3, 1/2, and 1/3 of the average cotton fiber diameter and 3/4, 1/2, and 1/3 of the average SMS fiber diameter when thermal diffusion lengths from Table 46 are considered. Information concerning the penetration of pesticides into fibers was obtained by comparing one absorption band (in the 1000 cm^{-1} region) in spectra collected from a single sample but collected using the following three interferometer optical velocities: 0.158, 0.317 and 0.633 cm/s. Information concerning the penetration of pesticides into fabrics was obtained by comparing one absorption band in spectra collected using the same optical velocity from the following samples: contaminated fabric face, fabric back, and the fabric powder made by grinding a whole fabric piece into a powder.

Since photoacoustic signal intensity is somewhat dependent on the physical state of a sample, all absorption bands from pesticides were normalized to absorption bands from fibers in the same spectra. This was accomplished by computing ratios composed of the intensity of an absorption band resulting from a pesticide divided by the intensity of an absorption band in the same spectrum resulting from the fiber substrate. These absorption band ratios provide a semi-quantitative measure of pesticide concentration since more pesticide would result in a larger peak ratio.

Results and Discussion

Unfinished Cotton--

Numerical values of FTIR/PAS peak ratios for unfinished cotton samples are presented in Table 47 and atomic concentrations computed from XPS spectra are presented in Figures 30-32 and Figures 28-29.

Table 47. PEAK RATIOS - FTIR/PAS SPECTRA: COTTON

Fabric Region Analyzed	Velocity(cm/s)	Uncontaminated Dicofol		Contaminated Terrazole®	
		829/897	923/897	829/897	923/897
Face	0.158	0.663	0.851	0.770	0.861
Face	0.317	0.664	0.855	0.772	0.861
Face	0.633	0.665	0.856	0.770	0.881
Back	0.317	---	---	0.736	0.850
Powder	0.317	---	---	0.803	0.912

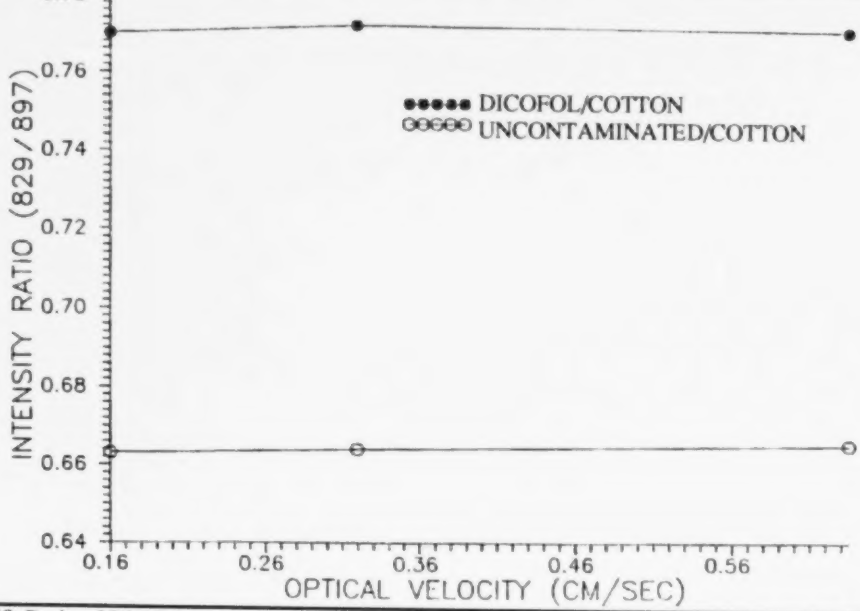


Figure 28. Ratio of Dicofol peak intensity to cotton peak intensity versus optical velocity for the fabric face.

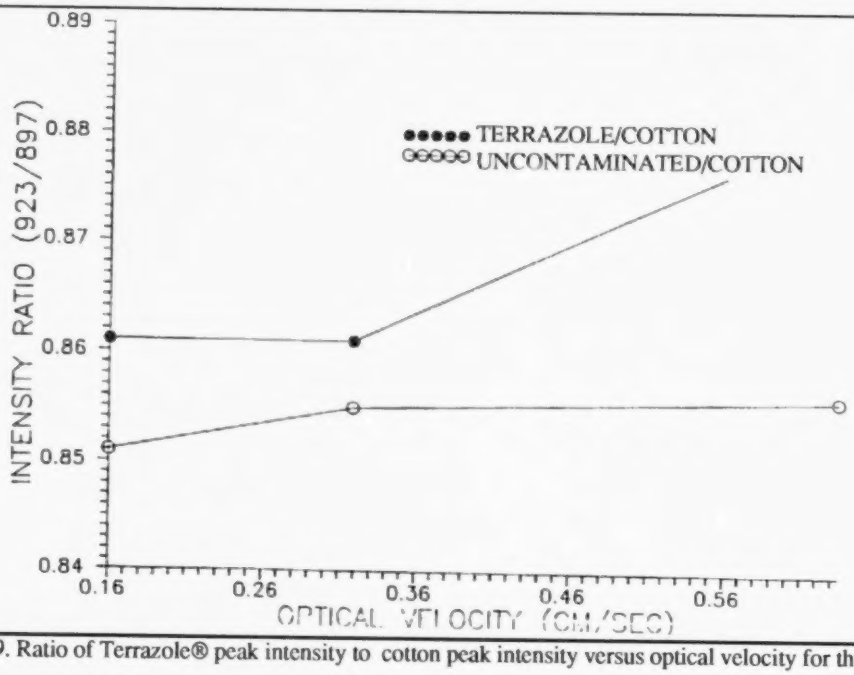


Figure 29. Ratio of Terrazole® peak intensity to cotton peak intensity versus optical velocity for the fabric face.

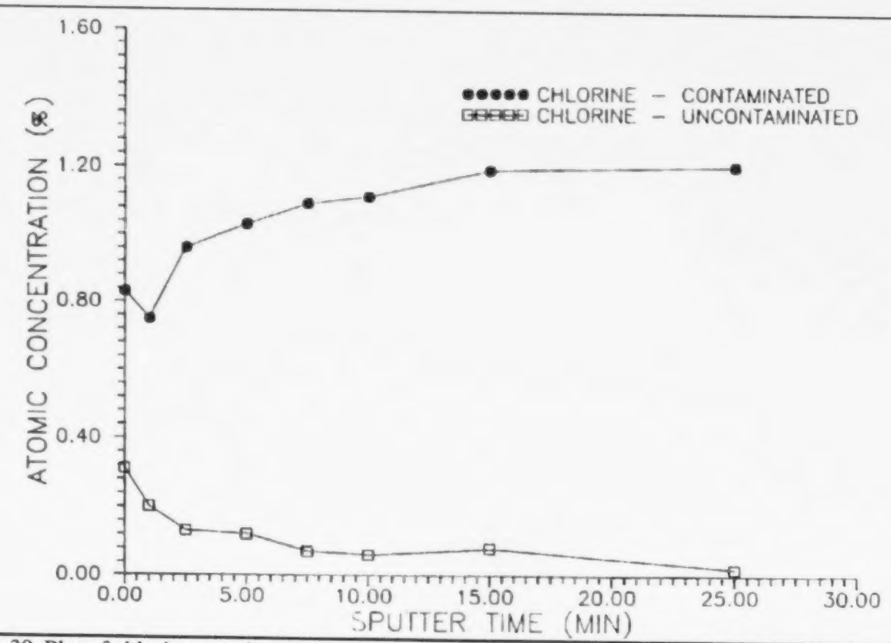


Figure 30. Plot of chlorine atomic concentration versus argon ion sputter time : diluted dicofol - cotton.

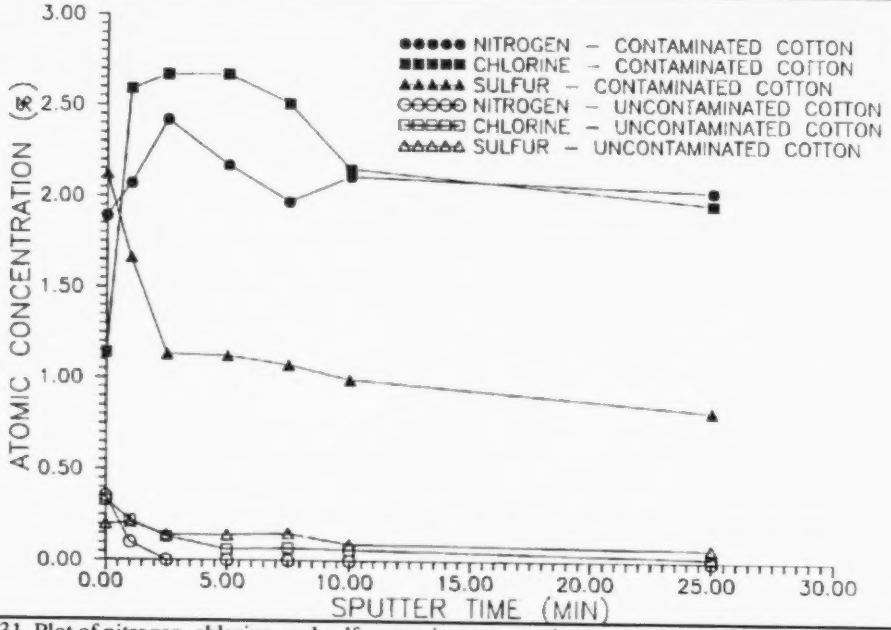


Figure 31. Plot of nitrogen, chlorine, and sulfur atomic concentrations versus argon ion sputter time: concentrated Terrazole® - cotton.

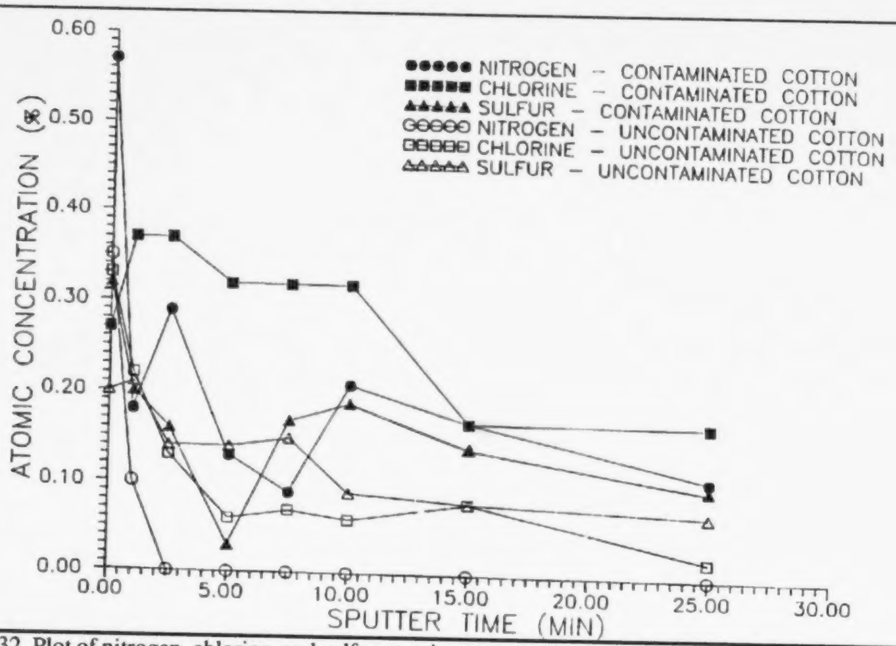


Figure 32. Plot of nitrogen, chlorine, and sulfur atomic concentrations versus argon ion sputter time : diluted Terrazole® - cotton.

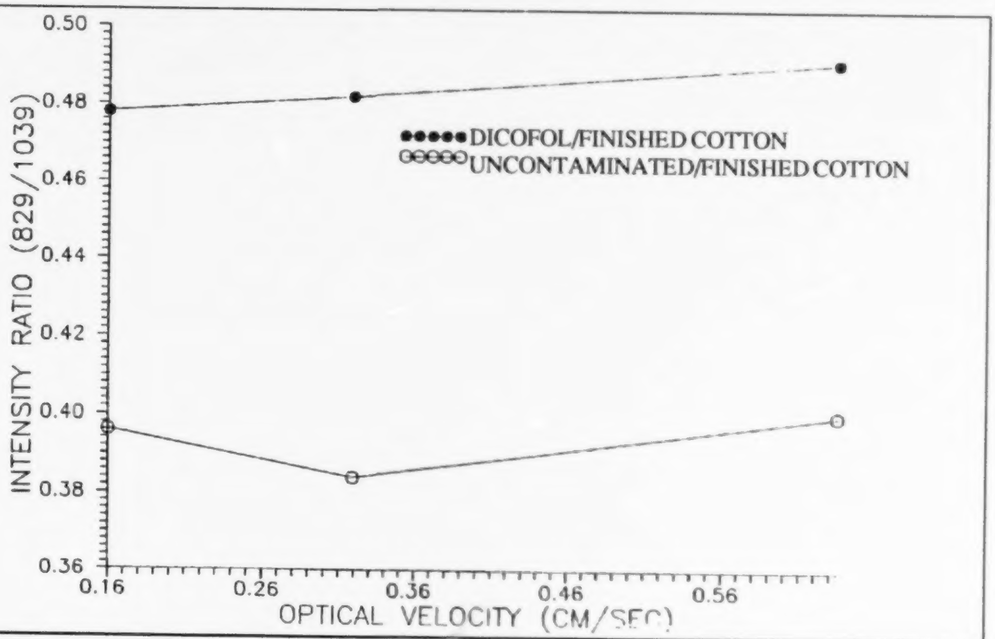


Figure 33. Ratio of Dicofol peak intensity to finished cotton peak intensity versus optical velocity for fabric face.

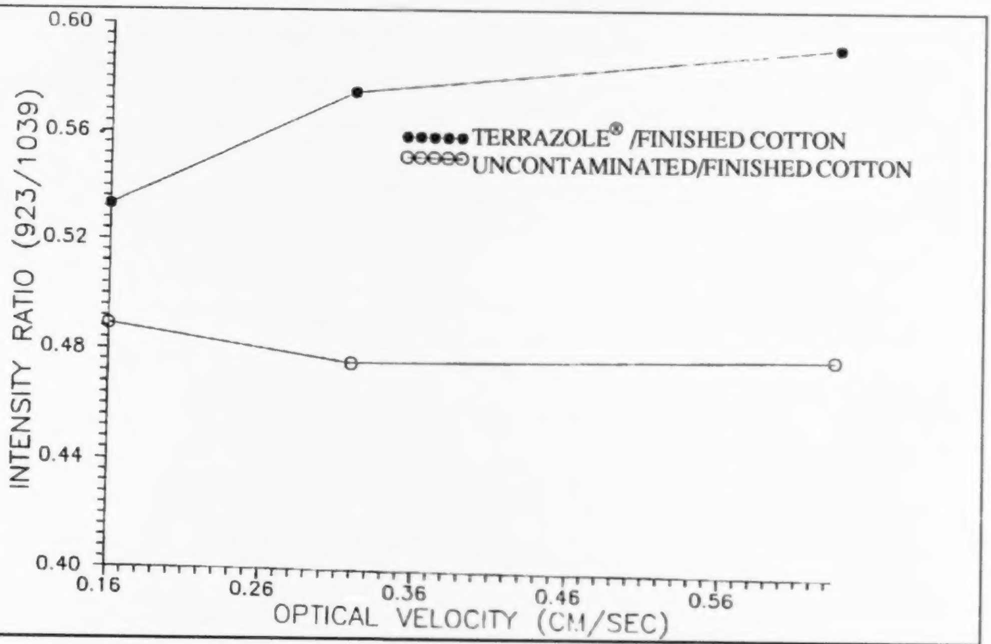


Figure 34. Ratio of Terrazole® peak intensity to finished cotton peak intensity versus optical velocity for fabric face.

A comparison of the 0.317 cm/s FTIR/PAS peak ratios in Table 47 (fabric face, fabric back, and ground fabric) suggests that the Terrazole® and Dicofol were located throughout the fabric and penetrated completely through the cotton fabric structure when applied as dilute sprays. However, the fabric back contained the least amount of the pesticides whereas the greatest pesticide concentrations were located in the interior of the fabric structure.

The XPS data shown in Figures 30-32 and FTIR/PAS data shown in Table 47 and Figures 28-29 for the fabric face show that Terrazole® applied as either a dilute spray or undiluted pesticide and Dicofol applied as a dilute spray remained on the surface of the cotton fibers but also were absorbed into the interior of the fibers. The concentration gradients associated with the pesticides indicate that absorption occurred readily and Dicofol was absorbed more easily than Terrazole®. The data indicate that cotton fibers behaved as a "sponge" that readily absorbed the two pesticides.

These findings suggest that, although the structure of the cotton fabric examined in this work allowed both pesticides to penetrate through the whole fabric thickness, cotton fibers in another fabric structure might possibly provide dermal protection against these two pesticides by containing pesticides through absorption. However, a fabric structure different than the one examined in this work must be employed to achieve protection. A suitable fabric structure might be one that did not allow liquids to flow through the fabric so that the pesticide remained on the outer fabric surface and was absorbed by the fibers.

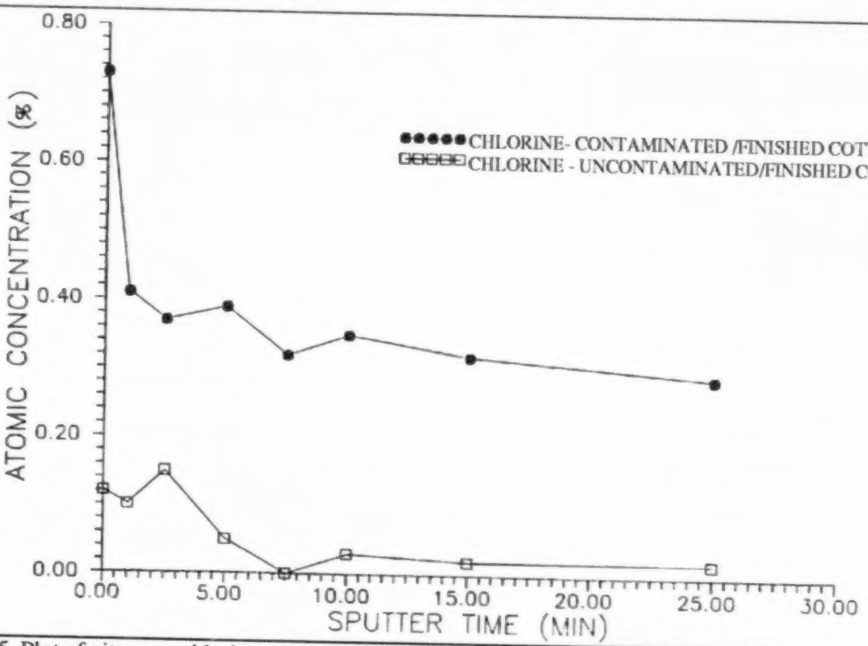


Figure 35. Plot of nitrogen, chlorine, and sulfur atomic concentrations versus argon ion sputter time: diluted Dicofol - finished cotton.

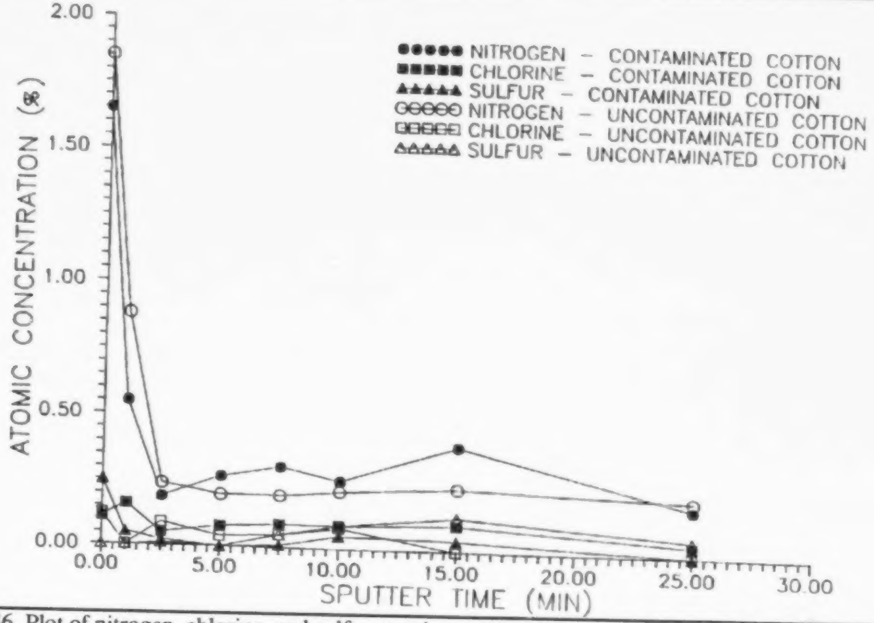


Figure 36. Plot of nitrogen, chlorine, and sulfur atomic concentrations versus argon ion sputter time: diluted Terrazole®- finished cotton.

Finished Cotton--

Numerical values of FTIR/PAS peak ratios for finished cotton samples are presented in Table 48 and Figures 33-34, and atomic concentrations computed from XPS spectra are presented in Figures 35-36. A comparison of the 0.317 cm/s FTIR/PAS peak ratios in Table 48 (fabric face, fabric back, and ground fabric) indicates that Terrazole® and Dicofol penetrated completely through

Table 48. PEAK RATIOS - FTIR/PAS SPECTRA: FINISHED COTTON

Intensity Ratio		Uncontaminated		Contaminated	
Fabric Region Analyzed	Optical Velocity(cm/s)	829/1039	923/1039	Dicofol 829/1039	Terrazole® 923/1039
Face	0.158	0.396	0.489	0.478	0.533
Face	0.317	0.384	0.476	0.482	0.576
Face	0.633	0.400	0.480	0.491	0.595
Back	0.317	0.363	0.462	0.399	0.485
Powder	0.317	0.481	0.557	0.504	0.584

the fabric structure when applied as dilute sprays. However, the fabric back contained the least amount of the pesticides whereas the greatest pesticide concentrations were located in the fabric interior. This behavior was similar to that of unfinished cotton fabric.

The XPS data shown in Figure 35 and FTIR/PAS data shown in Table 48 and Figure 33 for the fabric face indicate that Dicofol applied as a dilute spray remained on the surfaces of the fluorocarbon treated fibers but also was absorbed into the interior of the cotton fibers. In contrast, the XPS data in Figure 36, and FTIR/PAS data in Table 48 and Figure 34 shows that Terrazole® did not remain on the outermost fabric surface but was absorbed deeper into the fabric structure.

When these findings are compared to those of unfinished cotton, they indicate that the fluorocarbon finish had some effect on pesticide surface deposition. However, the fluorocarbon finish did not eliminate penetration of either pesticide through the fabrics. One possible benefit of fluorocarbon finishes suggested by this study is the reduction of secondary contamination through contact with contaminated textiles since the finish reduced deposition on the outermost fabric surface for one pesticide (Terrazole®).

SMS--

Numerical values of FTIR/PAS peak ratios for SMS samples are presented in Table 49 and Figures 37-38, and atomic concentrations computed from XPS spectra are presented in Figures 39-41.

A comparison of the 0.317 cm/s FTIR/PAS peak ratios in Table 49 (fabric face, fabric back, and ground fabric) indicates that resistance of the SMS fabric to penetration of Terrazole® differed markedly from that of Dicofol. That is, the SMS fabric acted somewhat as a barrier to Terrazole® penetration but allowed Dicofol to penetrate through the fabric structure. However, the distribution of Dicofol in the fabric structure was similar to pesticides distribution in the other fabrics in that the least amount of Dicofol was found in the fabric back whereas the greatest amount was located in the interior of the fabric structure.

The XPS data shown in Figures 39-41 and FTIR/PAS data shown in Table 49 and Figures 37-38 for the fabric face indicate that Terrazole® and Dicofol remained on the surfaces of the SMS fibers but both pesticides also were absorbed into the fiber interior. The data indicate that Dicofol is absorbed into the fibers substantially more readily than Terrazole®.

These findings show that the SMS fabric exhibited mixed behavior in limiting pesticide penetration through the fabric. That is, penetration was greatly limited for one but not for the other pesticide. SMS fibers also exhibited mixed behavior in pesticide absorption. This suggests that SMS has some potential to provide dermal protection, but combinations of SMS with some other textiles in a composite is indicated.

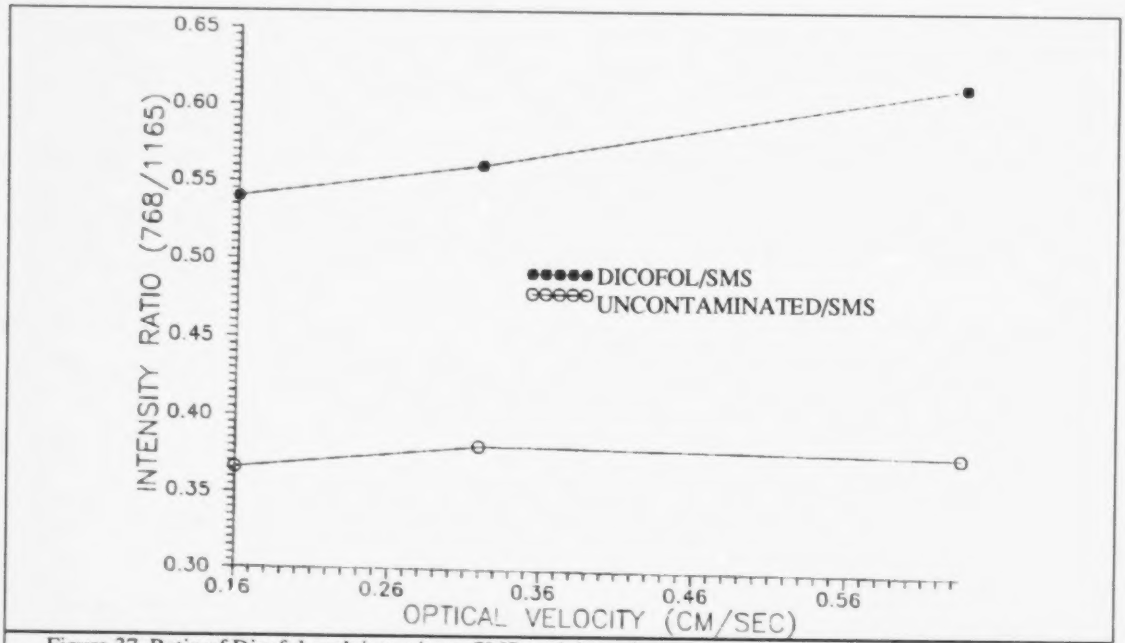


Figure 37. Ratio of Dicofol peak intensity to SMS peak intensity versus optical velocity for the fabric face.

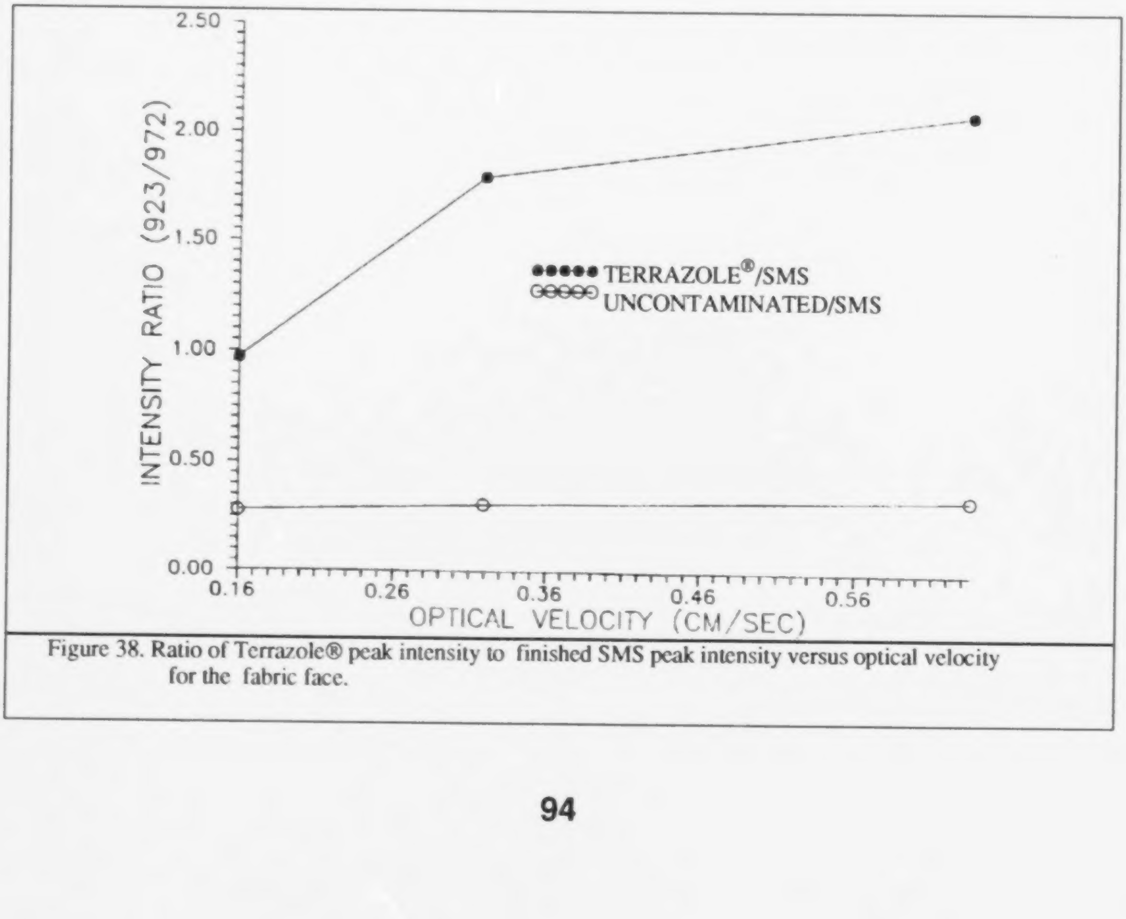


Figure 38. Ratio of Terrazole® peak intensity to finished SMS peak intensity versus optical velocity for the fabric face.

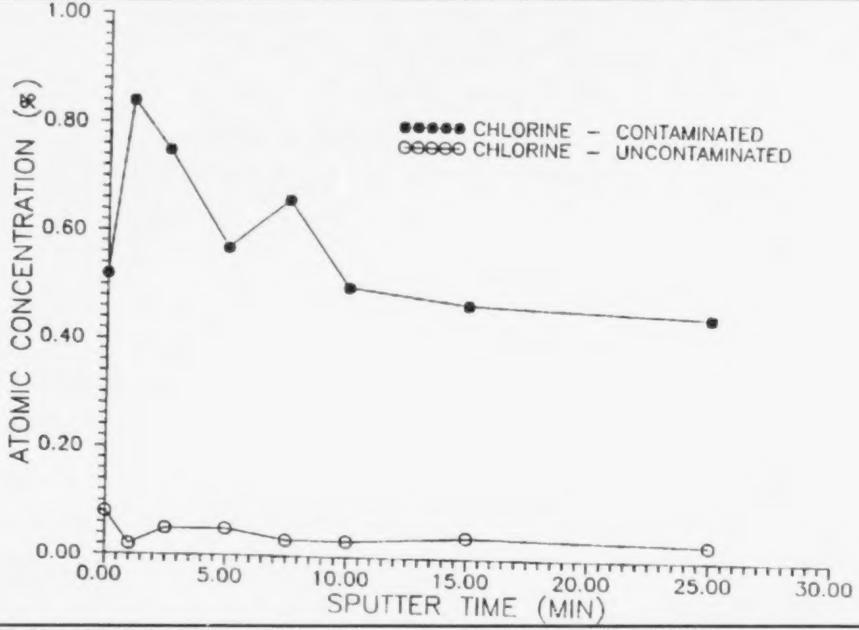


Figure 39. Plot of chlorine atomic concentrations versus argon ion sputter time: diluted Dicofol - SMS.

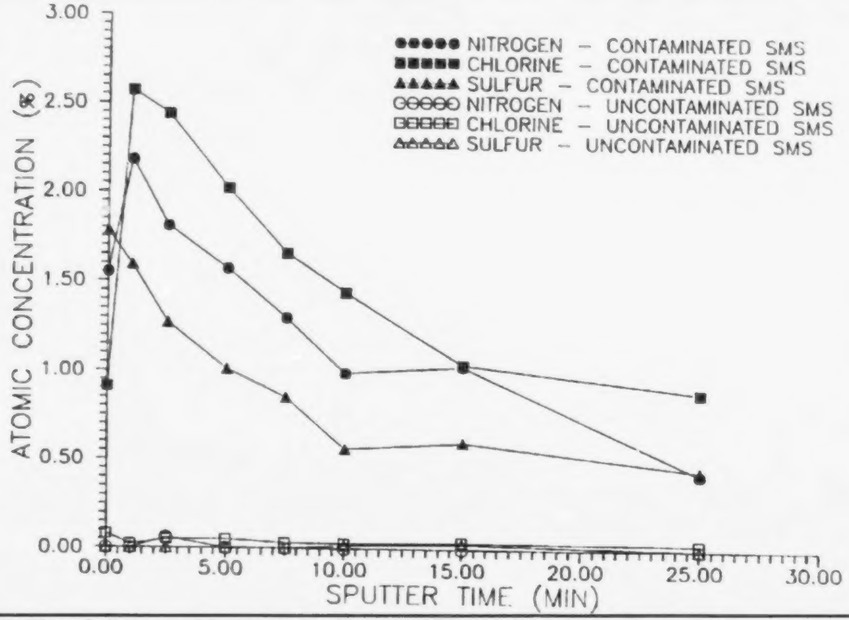


Figure 40. Plot of nitrogen, chlorine, and sulfur atomic concentrations versus argon ion sputter time: concentrated Terrazole®-SMS.

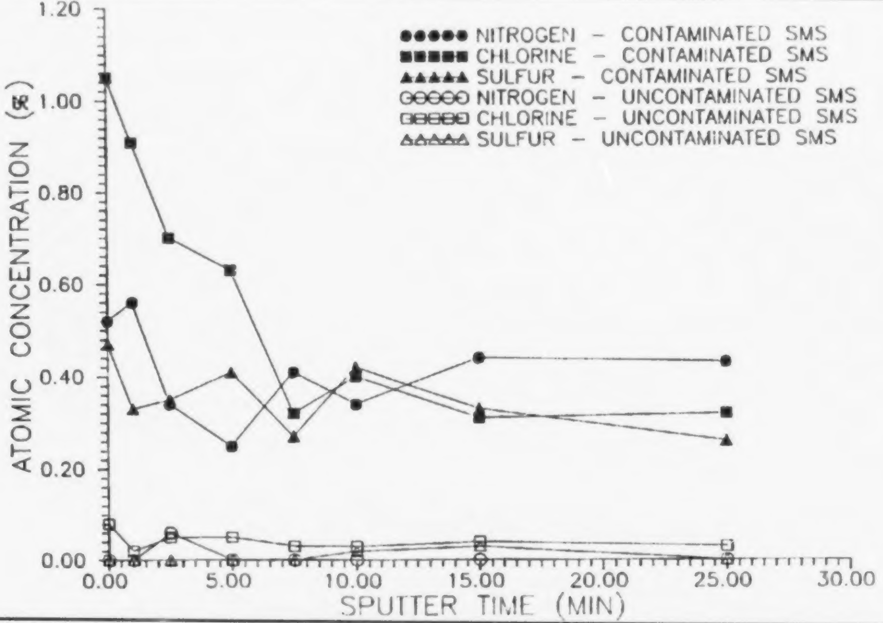


Figure 41. Plot of chlorine, nitrogen, and sulfur atomic concentrations versus argon ion sputter time: dilute Terrazole ® - SMS.

Table 49. PEAK RATIOS FTIR/PAS SPECTRA:SMS

		Uncontaminated		Contaminated	
		Dicofol		Terrazole	
Fabric Region Analyzed	Optical Velocity (cm/s)	768 1165	923 972	768 1165	923 972
Face	0.158	0.366	0.277	0.540	0.970
Face	0.317	0.381	0.310	0.562	1.795
Face	0.633	0.378	0.344	0.617	2.097
Back	0.317	0.426	0.387	0.553	0.402
Powder	0.317	-	-	0.630	0.314

SECTION 6

THERMAL COMFORT ASSESSMENT

The development of protective apparel for pesticide application has long been hampered by the often contradictory requirements to provide adequate protection against pesticide penetration and thermal comfort in conditions of high temperature and humidity. As pesticide penetration work continues to identify acceptable fabrics, attention must be paid to the thermal characteristics of these fabrics to make final recommendations of the fabrics that provide relative comfort in heat stress. If this is not accomplished, the agricultural workers will continue to choose not to wear the available protective apparel.

Thermal comfort testing has been conducted in several ways: (1) in a controlled laboratory setting by testing the fabric alone (20); (2) in a controlled environmental chamber using human subjects (12); (3) in actual human subject field testing conditions. The latter two are extremely expensive and should be used only after fabric has been properly screened for expected thermal performance.

The maintenance of thermal balance may be the most important physical comfort attribute of apparel. This balance is complicated when protective clothing is used in the high heat stress environments encountered in pesticide application. The textile must allow sufficient dissipation of body heat. In a field situation, heat is transferred by dry heat flow, evaporative losses and by air mass exchange or infiltration of outside air via air permeation due to wind. A problem exists in protective clothing for pesticide application in that the fabric properties conducive to chemical penetration protection are detrimental to textile properties which promote high heat dissipation. The requirement of keeping out liquids and/or particles tends to be incompatible with the necessity for air and moisture permeability.

Specific heat values determined using a differential scanning calorimeter exhibit minor changes in specific heat which are typically weak parameters in assessing the probable heat dissipation propensity of a specific textile over a range of ordinary temperatures and humidity levels. The surface temperature of apparel fabrics determined at various humidity levels and temperature ranges has been correlated with heat flux but requires further information regarding the heat source and moisture transport to justify the possible use of surface temperature to rate heat transfer of varied textile structures.

Therefore, the laboratory screening for the thermal performance of the fabric was assessed using direct tests which physically measure (1) thermal dissipation with (2) simultaneous moisture transport and (3) heat transfer augmentation due to wind induced air mass exchange.

EXPERIMENTAL PROCEDURE

Fabric

Fourteen woven and seven nonwoven fabrics were evaluated for thermal comfort in this laboratory screening. The fabric coding and descriptions are summarized in Table 49.

Table 50. FABRIC DESCRIPTIONS: THERMAL STUDY

Code	Common Name	Description
W1	Poplin	cotton, plain weave
W3	Broadcloth	cotton, plain weave
W5	Broadcloth	cotton, plain weave
W7	Duck	cotton, plain weave
W9	Print Cloth	cotton/polyester, plain weave
W11	Twill	cotton, twill weave
W13	Twill	cotton, twill weave
W14	Twill	cotton, twill weave
W15	Twill	cotton/polyester, twill weave
W16	Twill	cotton/polyester, twill weave
W21	Twill	cotton/polyester, twill weave
W22	Twill	cotton/polyester, twill weave
W23	Chambray	cotton/plain weave
W25	Denim	cotton, twill weave
N1	Tyvek®	polypropylene, nonwoven
N3	Sontara	polyester/wood pulp, nonwoven
N5	New Sontara	polyester/wood pulp, nonwoven
N7	SMS	polypropylene, nonwoven
N9	SMS	polypropylene, nonwoven
N11	SMS	polypropylene, nonwoven
N13	Gore Tex ®	composite, woven/nonwoven/knit

Laboratory Thermal Test Battery

A battery of comfort-related physical tests were used to assess the ability of experimental protective clothing fabrics to relieve the heat stress developed during summer-time pesticide application work. Three physical measurements were performed on the fabrics: thermal transmittance (U-values), wind penetration potential (WPP), and the clothing radiant temperature (Clort).

U-Values--

Fabric thermal transmittance (U-value) is a measure of the total heat flow through the fabric per unit temperature difference across the air layers on each side of the fabric. U-value units are W/m^2K

or BTU/hour/square foot/Deg. Fahrenheit. U-values were measured during simultaneous moisture transport to reflect the ability of the fabrics to transport heat under simulated sweating, heat stress conditions (21).

A guarded heat and mass transmittance test instrument measures thermal transmittance of flat fabrics under a mixed flow state of free convection (20). The Mixed Flow Transmittance Tester (MFTT) uses solid state heat flow transducers situated on large flat plate heat sinks that are critically spaced, guarded, and temperature controlled. Mixed flow is a distinctive state of heat transfer for which the ratio of total transmittance to the conductive heat flow across an air space is constant. This controlled, natural convection feature makes it possible to standardize thermal transmittance results under defined free convective conditions. Water reservoirs made with silicone caulk levees were placed on the heat source plate to serve as a moisture generator. The water surface area was one half the plate area. The cold plate served as a condensing chill plate for the transported moisture as its temperature was always less than the dew point of the adjacent air mass. The moisture generating system was designed to produce a constant vapor supply for transport through the air and textile being tested. The mixed flow convective state produced in the apparatus was expected to prevent vapor stratification in the chambers.

At heat stress conditions, U-Values of apparel fabrics can range from 8.5 to 14.2 W/m^2K. On initial exposure to "sweating" heat stress conditions in the MFTT, fabrics generally condense some moisture while transmitting heat and moisture through the fabric. The maximum U-Value attained is affected by the ability of the fabric to maintain high moisture flux and on its physical characteristics related to effective thickness. Hairiness, texture and wicking affect surface temperatures and the location and type of moisture condensation produced.

In a U-value determination, water was added to reservoirs on the heat source plate, excess condensation was removed from the chilled top plate, and the fabric specimen was inserted between the MFTT halves. Temperature and heat flux signals were converted to U-values by a data acquisition system which also plotted the results. Values of the initial U-value and equilibrium values were recorded. The initial value indicates the initial comfort response (high U implying grater relief of heat stress). Equilibrium U-values were expected to reflect the ongoing ability of the fabric to transfer heat away from a sweating subject.

Wind Penetration Potential--

The Wind Penetration Potential (WPP) was designed to characterize the heat stress relief benefit of wind. The WPP of the fabric is defined as the area under a graph of the air flow rate through a fabric over a range of differential pressure across the fabric. The WPP for a fabric assesses the potential for wind (or tractor movement) to reduce "on the job" heat stresses with respect to the chambray. The WPP parameter is supported by other work on wind effect reviewed by Fourt and Hollies (22) and the recent aerial penetration work of Harter et al (23) and others (24,25,26) using tracer gas techniques to assess microclimate air exchange due to wind. A Gurley Densiometer/-Permeometer was modified and automated to plot air flow as the differential pressure across the fabric was varied. The Gurley Densiometer/Permeometer is a standard testing method for air permeability as measured at 124.9 Pascal. Whereas this technique measures air permeability at one pressure drop, the modified technique used here (WPP) integrates the permeability performance over a range of pressures. Wind-induced pressures vary with wind speed and are nonlinear. That range assesses the wind penetration at low through high wind velocities, thus more closely simulating the cooling effect wind may have passing through various fabrics.

Clothing Radiant Temperature (Clort)--

The test battery further includes an "instrumental operative temperature" parameter which assesses the radiant temperature field to which the skin of the clothed subject in a controlled environment is exposed (27). The Clort is affected by the clothing and the microclimate to which the wearer's skin (heated plate) is exposed. The parameter is named the clothing radiant temperature or Clort, as it assesses the effect of the clothing on the radiant field to which the "skin" is exposed for a controlled external environment. Conventional woven fabrics transmit radiant heat as a function of their cover. In a given environment, the Clort parameter simulates the mean radiant temperature (heat) signal felt by the skin as seen through the clothing. This thermal stimulus activates one's physiology to react to the thermal environment. As an element of the thermal test battery, a higher Clort value is interpreted as a hotter environment to the skin, potentially contributing to or signalling the onset of thermal discomfort.

The infrared thermometer and front surface mirror assembly is built into one side of the MFFT instrument. Clort measurements are taken concurrent with thermal transmittance testing. The infrared radiant temperature of the fabric is measured from the warm-air side of the fabric.

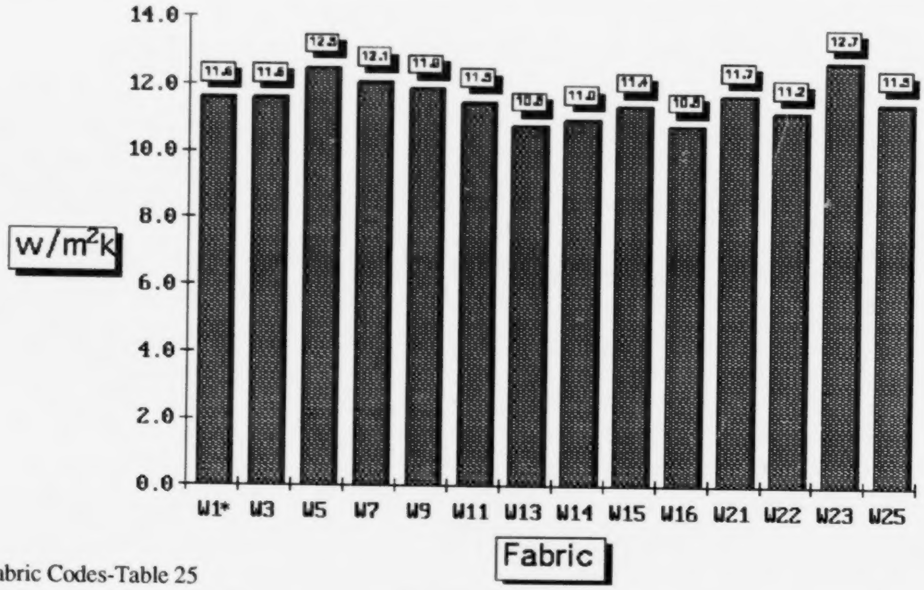
Experimental Results

Thermal Test Battery--

The overall thermal performance rating of the group of fabrics was assessed relative to performance in a high-heat stress pesticide application environment. Fabric W23, a shirt-weight chambray fabric, was used as a reference point for evaluating the relative comfort level of the other test fabrics and for developing rating scales based upon all three thermal measures.

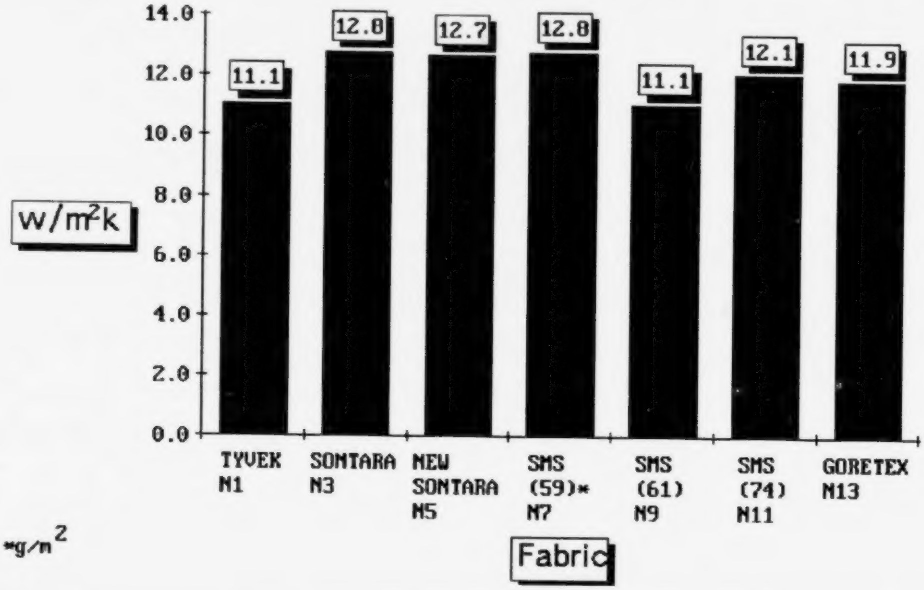
U-Values--

U-Values were converted to U-scores by a linear relationship based upon U-values of 5.68 w/m2K and 12.70 w/m2K corresponding to scores of 0 and 10 respectively. Thermal transmittance U-value responses ranged from 10.8 to 12.7 in woven fabrics (Figure 42) and 11.1 to 12.8 in nonwoven fabrics (Figure 43). The standard cotton chambray (W23) received a high U-value of 12.7 which relieves the most heat stress. Sontara® and SMS performed as well as Chambray. Tyvek® and heavy-weight woven fabrics were the poorer performers.



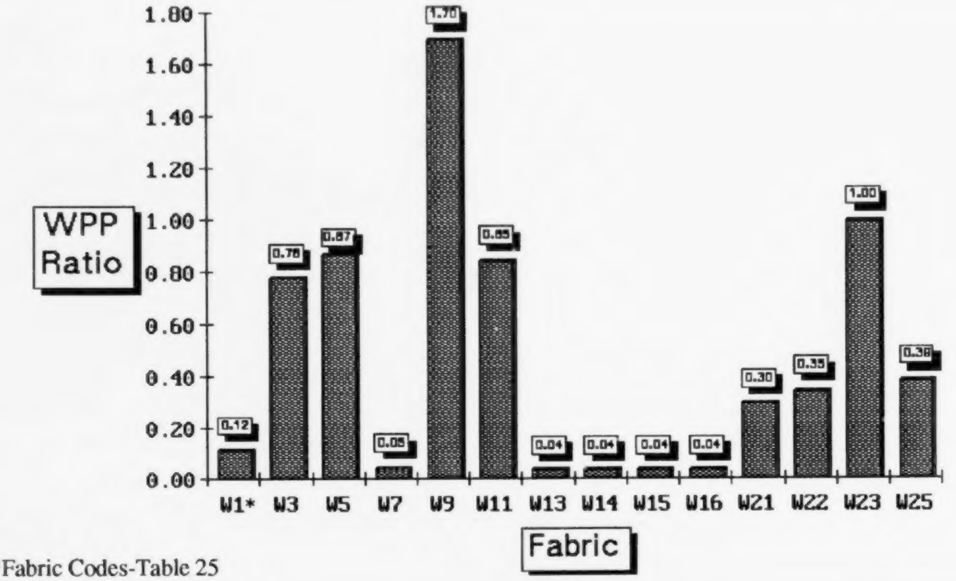
*Fabric Codes-Table 25

Figure 42. Thermal Test Battery Results U-Value: Woven



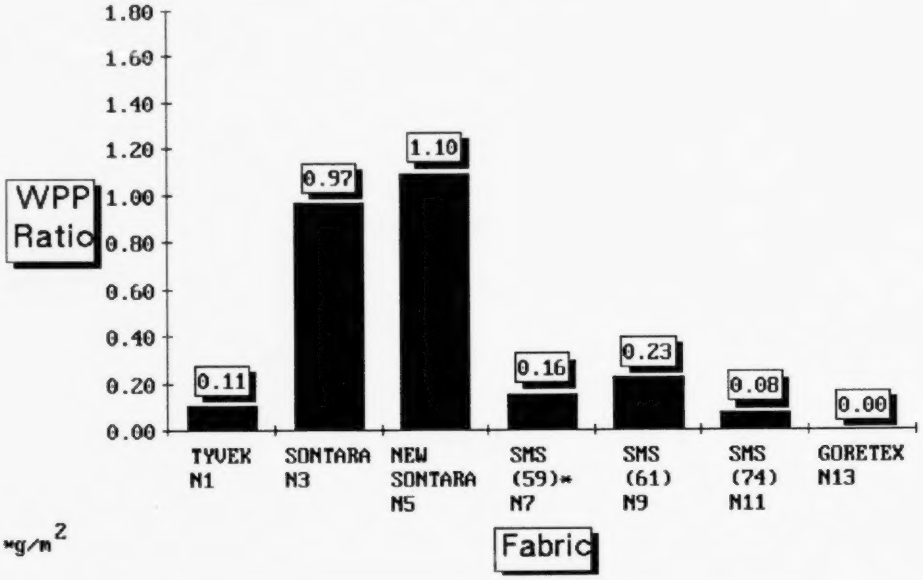
*g/m^2

Figure 43. Thermal Test Battery Results U-Value: Nonwovens



*Fabric Codes-Table 25

Figure 44. Thermal Test Battery Wind Penetration:Woven



*g/m^2

Figure 45. Wind Penetration:Nonwovens

WPP Values--

WPP Values reflect the "airiness" or potential benefit of light breezes to improve the thermal comfort of the fabric. Nonpenetrating wind effects a generally constant increase in the heat transfer from a nude or heavily clothed body. Fabric permeability alters the base levels of heat that can be removed by wind effect. The area under the WPP curve was used as the WPP-value. With cotton chambray having the standardized rating of 1.0, the woven fabrics ranged from 0.4 for heavier weight to 1.7 for lighter weight cotton (Figure 44). The nonwoven fabrics ranged from 0.0 (Gore Tex®) to 1.1 (new Sontara) (Figure 45). A WPP score was computed by multiplying the WPP value by 10.0 to equalize its weighting with the other tests in the thermal battery.

High WPP-score fabrics generally had the higher U-values but exhibited a wide range in the Clort parameter. Relative to the low WPP-value group, the twill fabrics had low flow properties characteristic of their tightly woven staple yarn construction. SMS had lower air permeability values over the pressure range due to the microporous texture of the melt blown "M" component. Gore Tex® film has very low air permeability due to submicron pore structure.

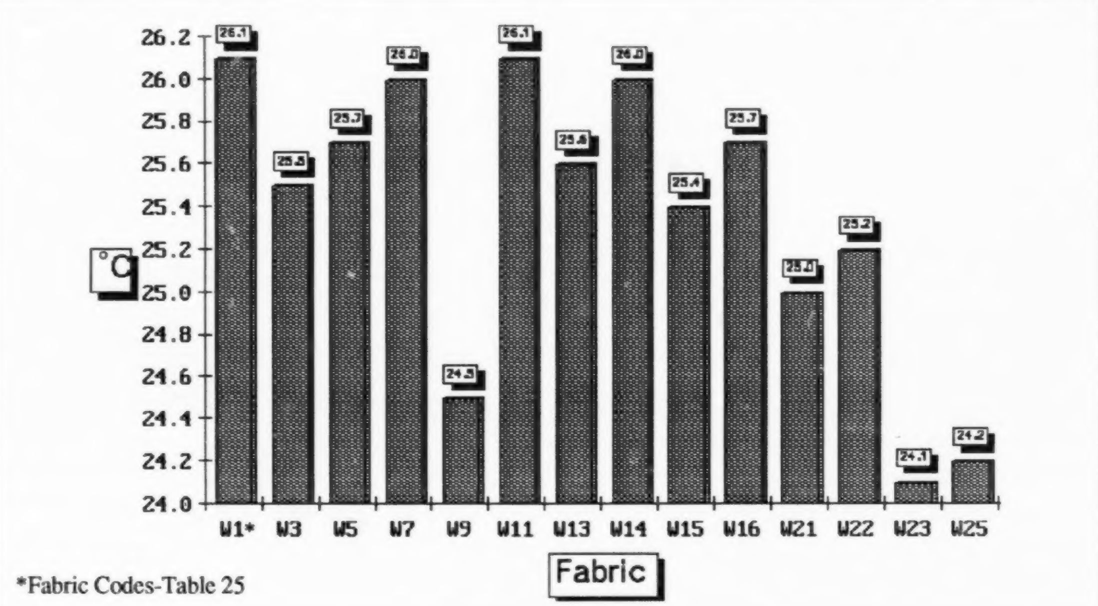
Clort--

The Clothing Radiant Temperature, or Clort, was defined as a reference mean radiant temperature that the skin sees (comfort sensation with the clothing). The lower the Clort value, the higher the clort score and the lower the heat stress on the skin. An inverse linear relationship with 24° or less and 29° or above, representing scores of ten and zero respectively, was used to convert Clort values to Clort scores. The woven fabrics ranged in Clort value from 24.1 to 26.1°C (Figure 46). Chambray (W23) had a low value of 24.1°C. Untreated twill (W21) and Gore Tex® (N13) had equal values of 25.00C; treated twill was slightly higher at 25.2°C. The nonwoven fabrics' Clort values ranged from 21.3 (Tyvek®) to 25.8 (SMS) (Figure 47).

The Clort values were influenced strongly by the condensation behavior of the fabric. Condensation creates localized absorptive heating (23), possibly accounting for the lower Clort values for fabrics that exhibited condensation on the fabric back, such as Tyvek®. Fabric transparency to long wave infrared radiation would reduce the Clort values measured. In effect, the skin would be radiated by the warm fabric clothing and a cooler background radiating through the fabric.

Discussion

Fabrics earning the highest overall heat stress relief scores (HSRS) beginning from highest ranking are W9 (light weight cotton), W23 (cotton chambray), N5 (Sontara), and N3 (Sontara) (Table 50) (Figure 48) (Note: N3 and N5 are two slightly different weights of the same fabric, 59 g/m2 and 61 g/m2). In general, the rating in the WPP parameter produced the major differentiation among the high ranking fabrics. Fabrics generally impermeable to air flow at the low pressures produced by windy environmental conditions (e.g. N1, W13, W15, N13, etc) will be deficient in the relief of the high heat stress produced in the environment considered above.



*Fabric Codes-Table 25

Figure 46. Thermal Test Battery Results CLORT: Woven

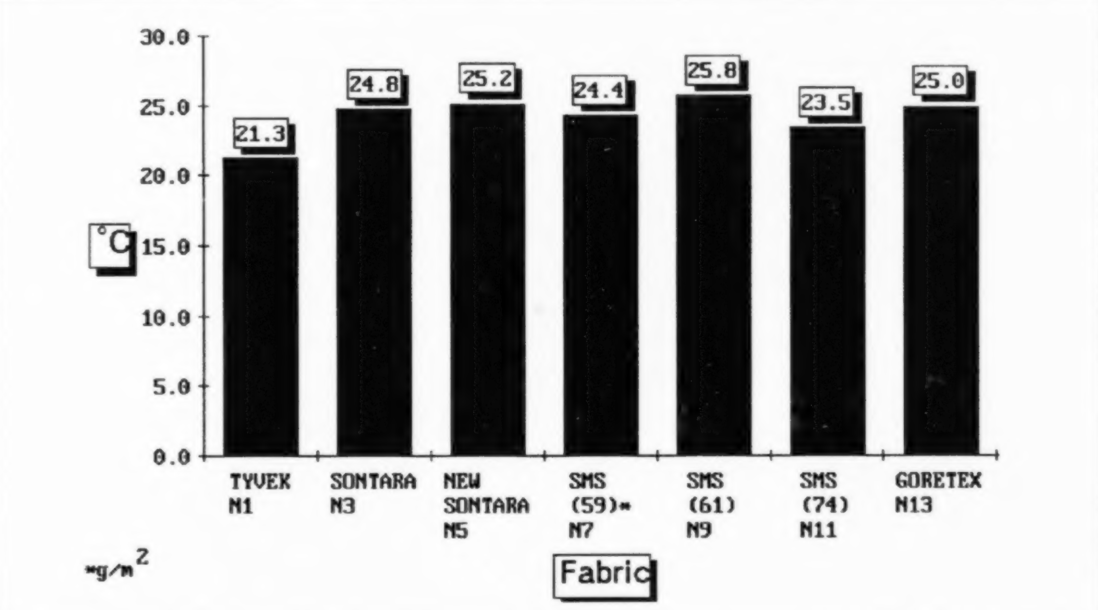
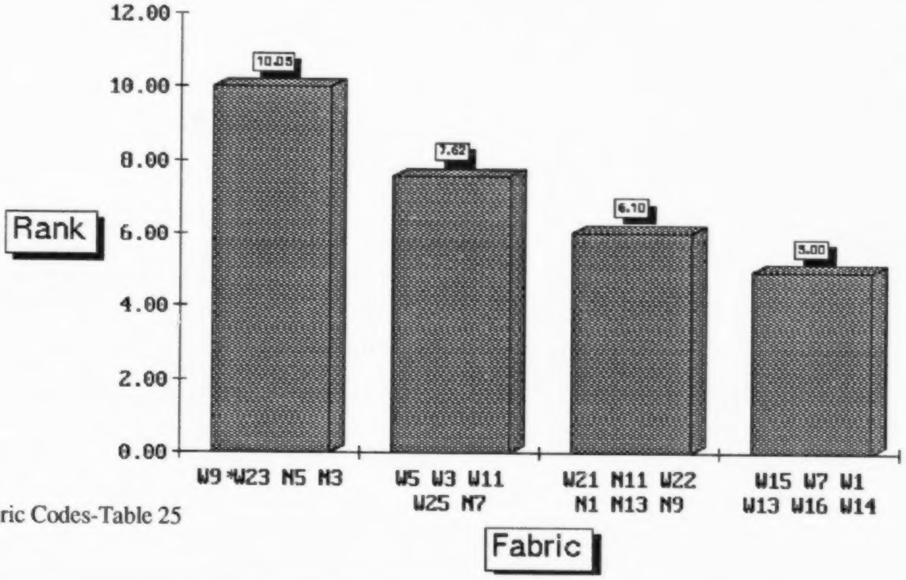


Figure 47. Thermal Test Battery Results CLORT: Nonwoven

Table 51. HEAT STRESS RELIEF SCORE RANKINGS

Rank	Code	Fabric	Normalized Score
1	W9	Print Cloth	11.6
2	W23	Chambray	10.0
3	N5	New Sontara	9.6
4	N3	Sontara	9.4
5	W5	Broadcloth	8.4
6	W3	Broadcloth	7.8
7	W11	Twill	7.6
8	W25	Denim	7.3
9	N7	SMS	7.0
10	W21	Twill	6.6
11	N11	SMS	6.6
12	W22	Twill	6.4
13	N1	Tyvek®	5.9
14	N13	Gore Tex ®	5.6
15	N9	SMS	5.5
16	W15	Twill	5.3
17	W7	Duck	5.3
18	W1	Poplin	5.2
19	W13	Twill	4.8
20	W16	Twill	4.8
21	W14	Twill	4.7



*Fabric Codes-Table 25

Figure 48. Heat Stress Relief Scores

The U-value gives the rate at which the fabric can transmit heat and moisture related heat through the fabric. Fabrics having the highest HSRS's generally had U-values greater than 12 W/m (2.12 BTU/h ft2F), which converts to a U-score of 7.0. Fabric N13 had a respectable U-value of 11.9 W/m yet had no ability for heat exchange due to wind penetration as assessed by the WPP test. Other fabrics that exhibited high WPP values, such as W21, W22, and N9, had relatively low U-values, due to the condensation behavior of these fabrics. It was observed that condensation on the fabric formed a continuous layer on the fabric, possibly retarding moisture transport. A thin fabric having no vapor permeability has a U-value of about 8.5 W/m .

Conclusions

The combination of the three thermal laboratory tests used in this test battery differentiated thermal ratings among the fabrics evaluated. The normalized total scores ranged from 4.7 (W14) to 11.6 (W9). Those fabrics with the highest overall heat stress relief scores (HSRS) which provided comfort nearly equal to that of cotton chambray included both woven and nonwoven fabrics. The woven plain weave fabric which was lighter in weight and thickness than chambray was shown to have the highest HSRS. Sontara, which is made of a combination of polyester and wood pulp, had excellent HSRS ratings and shows great promise as comfortable, protective apparel. The thickest and heaviest twill fabrics (W13, W14, and W16) had the lowest HSRS ratings. In woven fabrics, fiber content did not appear to influence the comfort as both 100% cotton and 50/50 cotton polyester were included in this least comfortable grouping. SMS, Gore Tex®, and unfinished Tyvek® all have ratings similar to that of denim.

Therefore, based on these findings the thermal comfort laboratory test battery indicates weight and thickness of woven fabrics influence thermal performance. In nonwoven fabrics the addition of a natural fiber (wood pulp, in this case) appears to be the only factor in increasing the heat stress relief rating.

REFERENCES

1. Serat, W.F., Van Loon, A.J., and Serat, W.H. Loss of Pesticides from Patches Used in the Field as Pesticide Collectors. *Archives of Environmental Contamination and Toxicology*, Vol. 11, 1982, pp. 227-234.

2. Raheel, M. and Gitz, E.C. Effect of Fabric Geometry on Resistance to Pesticide Penetration and Degradation. *Archives of Contamination and Toxicology*, Vol. 14, 1985, pp. 273-279.

3. Orlando, J., Branson, D., Ayres, G., and Leavitt, R. The Penetration of Formulated Guthion® Spray Through Selected Fabrics. *Journal of Environmental Science and Health*, Vol. 5, 1981, pp. 617-628.

4. Easter, E.P. and DeJonge, J.O. The Efficacy of Laundering Captan and Guthion® Contaminated Fabrics. *Archives of Environmental Contamination and Toxicology*, Vol. 14, 1985, pp. 281-287.

5. DeJonge, J.O., Ayres, G., and Branson, D. Patterns of Pesticide Deposition of Clothing During Air Blast Spraying. *Home Economics Research Journal*, Vol. 14, No. 2, 1985, pp. 262-268.

6. Pratt, H.D. and Littig, K.S. The Relationship Between Insecticide Application and Particle Size. *Insecticide Application Equipment for* the Control of Insects of Public Health Importance, U.S. Department of Health, Education and Welfare Publication (CDC), 76-8273, 1974.

7. Staiff, D.C., Davis, J.E, and Stevens, E.R. Evaluation of Various Clothing Materials for Protection and Worker Acceptability During Application of Pesticides. *Archives of Environmental Contamination and Toxicology*, Vol. 11, 1982, pp. 391-398.

8. Leonas, K.K. and DeJonge, J.O. Effect of Functional Finish Barriers on Pesticide Penetration. *Performance of Protective Clothing*, ASTM Special Technical Testing Publication 900, R.L. Barker and G.C. Coletta, Eds., American Society for Testing and Materials, Philadelphia, 1986.

9. Freed, E.P., Davies, J.E., Peters, L.J., and Parveen, F. Minimizing Occupational Exposure to Pesticides: Repellency and Penetrability of Treated Textiles to Pesticide Sprays. *Residue Reviews*, Vol. 75, 1980, pp. 159-167.

10. Lillie, T.H., Livingston, J.H., and Hamilton, M.A. Recommendations for Selecting and Decontaminating Pesticide Application Clothing. *Bulletin of Environmental Contamination and Toxicology*, Vol. 27, 1981, pp. 617-628.

11. Kawar, N.W., Gunther, F.A., Serat, W.R., and Iwata, Y. Penetration of Soil Dust Through Woven and Nonwoven Fabrics. *J. Environ. Sci. Health*, Vol. B13, No. 4, 1978, pp. 401-415.

12. Branson, D.H., DeJonge, J.O., and Munson, D. Thermal Response Associated with Prototype Pesticide Protective Clothing. *Textile Research Journal*, Vol. 56, No. 1, 1986, pp. 27-34.

13. Minor, F.W., Schwartz, A.M., Buckles, L.C., Wulkow, E.A., Marks, M.P., and Fielding, G.H. The Migration of Liquids in Textile Assemblies, Part IV: Penetration of Fabrics by Liquids. *Textile Research Journal*, Vol. 31, 1961, pp. 525-539.

14. Maibach, H.I., Fieldman, R.J., Milby, T.W., and Serat, W.F. Regional Variation in Percutaneous Penetration in Man. *Archives of Contamination and Toxicology*, Vol. 23, 1971, p. 208.

15. Hays, W.L. *Statistics for the Social Sciences*, Holt, Rinehart and Winston and Co., New York, 1973, pp. 499-500.

16. Raheel, M. Pesticide Penetration in Fabrics: Fiber Chemistry Surface Energy and Fabric Porosity. *The First International Symposium on the Impact of Pesticides, Industrial and Consumer Chemicals on the Near Environment*, Ed. Barbara Reagan, Diana Johnson, Shailendra Dusaj, Kansas State University, Manhattan, Kansas, 1988, pp. 127-136.

17. Solbrig, C.M. and Obendorf, K. Distribution of Residual Pesticide within Textile Structures as Determined by Electron Microscopy. *Textile Research Journal*, Vol. 55, pp. 540-546.

18. Perkin Elmer Corporation, *5100 XPS Instruction Book*, 1988.

19. Rosencweig, A. *Photoacoustics and Photoacoustic Spectroscopy*, John Wiley, New York, 1980, pp. 84-98.

20. Fourt, L. and Harris, M. in *Physiology of Heat Regulation and the Science of Clothing*, L.H. Newburgh, Ed., Hafner, New York, 1968.

21. Hassenboehler, C.B., Jr. and Vigo, T.L. A Mixed Flow Thermal Transmittance Tester for Textiles. *Textiles Research Journal*, Vol. 52, 1982, pp. 510-517.

22. Fourt, L. and Hollies, N.R.S. The Comfort and Function of Clothing. Technical Report 69-74-CE, The United States Army Natick Laboratories, Natick, Massachusetts, 1969.

23. Harter, K.L., Spivak, S.M., Yeh, K., and Vigo, T.L. Application of the Trace Gas Technique in Clothing Comfort. *Textile Research Journal*, Vol. 51, 1981, pp. 345-355.

24. Stuart, I.M. and Denby, E.F. Wind Induced Transfer of Water Vapor and Heat Through Clothing. *Textile Research Journal*, Vol. 53, 1983, pp. 655-660.

25. Shivers, J.L. in *Clothing Comfort*, N.R.S. Hollies and R.F. Goldman, Eds., Ann Arbor Science Publishers, Michigan, 1977.

26. Spencer-Smith, J.L. The Physical Basics of Clothing Comfort, Part 3: Water Vapor Transfer Through Dry Clothing Assemblies, *Clothing Research Journal*, Vol. 5, 1976, pp. 82-100.

27. Gagge, A.P. A New Physiological Variable Associated with Sensible and Insensible Perspiration. *American Journal of Physiology*, Vol. 120, 1937, p. 277.

APPENDIX A

STANDARD OPERATING PROCEDURES

Sampling

All woven fabrics were pre-washed to remove impurities from routine finishing, according to the following procedure.

Pre-Laundering of Fabrics

- The washer and dryer are cleaned using an acetone rinse and dummy load.
- Four pounds (4 lbs) of fabric are weighed and loaded into washer.
- Washer settings checked to meet above specifications.
- Washer filled with H_2O (automatic fill) - high H_2O level.
- As agitation begins, add 1/2 cup liquid ALL detergent (approx. 100 ml) to washer.
- Allow wash/rinse cycle to complete.
- Run a second wash/rinse cycle without detergent (use same settings as before).
- Remove fabric from wash. Place in dryer and adjust to appropriate settings.
- Remove fabric when dry.

Assessment of the pesticide penetration through fabrics was accomplished by the use of a multi-layer fabric assembly. The four-layer composite, 15.2 cm x 15.2 cm square consisting of the test fabric, a collector layer, foil and foil backing. For this study, the test fabric is being evaluated for its ability to prevent pesticide penetration. The collector layer was a 50% cotton/50% polyester blended tee-shirt fabric supplied by Standard Knitting Mills of Knoxville, Tennessee. The four layers were prepared according to the following standard procedures.

Cutting of Fabric Samples and Specimen Assembly Cutting

Randomized cutting is completed according to ASTM 1682-64 test procedure.

Wrinkle free fabrics are laid out flat on a clean surface. (Wash fabrics before cutting if unfinished).

Using MA template of 15.2 cm x 15.2 cm square with 7.62 cm x 2.54 cm cutout, samples are marked in random order allowing 10% free fabric at each salvage edge.

A permanent marker is used to trace around template and 7.62 cm x 2.54 cm cutout (fabric ID is written in corner of square with permanent marker).

Samples are cut using clean scissors and stored in laboratory cabinets until ready for assembly.

Assembly of Specimens

- Multilayer samples consist of four layers arranged from top to bottom as follows:
- Test fabric (15.2 cm x 15.2 cm with 7.62 cm x 2.54 cm rectangle).
- Collector layer of 50/50 polyester/cotton jersey knit (washed in same manner as test fabrics).
- Aluminum foil (15.2 cm x 15.2 cm with 7.62 cm x 2.54 cm rectangle marked on dull side).
- Foil backing (15.2 cm x 15.2 cm with 7.62 cm x 2.54 cm rectangle marked on dull side).
- Place a foil square on a clean table with dull side facing down.
- Place a second foil layer on top of the first with dull side face down.
- Place a knit square on second foil layer with the side which has been marked with 7.62 cm x 2.54 cm MA rectangle facing down.
- Place a test fabric layer on top with the side marked with 7.62 cm x 2.54 cm rectangle facing up.
- Place 2.54 cm strips of double-stick tape at edges between each layer to hold the specimen together.
- Seal the edges of the specimen using 1" masking tape folding 1.27 cm on top layer and 1.27 cm bottom layer.

Contamination was achieved by subjecting fabric assemblies to a controlled enclosed spray chamber to one pass of the spray system. The following standard procedures were followed:

Spraying of Fabrics and Drying

Before spraying, the spray chamber is checked for proper operation. The system is checked for leaks using distilled water. The spray nozzle tip is positioned 30.48 cm (12") from the sample holder surface and the spray nozzle is checked for proper spray pattern. If any problems are found, they are corrected before spraying pesticides.

When spray nozzle is changed and before every new project, the spray nozzle is calibrated. Calibration is performed by placing watch glasses, 12.54 cm diameter, on fabric holders and inserting them into the spray chamber. Distilled water is then sprayed at 40 psi with a speed setting producing a rate of 4.72 cm per second. The weight of the watch glasses is recorded before and after spraying to obtain the weight of water sprayed. This is done several times to obtain an average and the amount of liquid per area is determined.

Before each day's spraying, the speed of the nozzle (rate of traverse) is checked for consistency (5%) and corrected if necessary.

The pesticide solution bottle is connected to the spray nozzle and to the compressed helium tank and is then pressurized at 40 psi. The spray is allowed to equilibrate and the pattern is checked while the nozzle is positioned at the far left of the spray chamber. The randomly placed samples are clipped to the fabric holders and inserted into the spray chamber. The spray nozzle is then passed over all four (4) samples and stopped. The spray is shut off and sample holders removed. All spraying is done from left to right. The samples are carefully removed from the sample holders and placed under an aluminum foil-lined hood in the same order that they were sprayed and allowed to dry for one hour with the hood fan running.

Fabric assemblies were removed from the chamber and dried in a vented hood for one hour. The fabric layers were then separated and cut according to the following routine procedures:

Sample Cutting, Extraction and Storage

Sample Cutting: After drying, the samples were removed from hood and one end of sample is cut off with scissors. The back foil layer is removed. The primary foil layer 1" x 3" marked area is cut out and placed in a labeled culture tube with a teflon lined cap. The knit layer marked area is cut out the same way and finally the test layer is cut. After cutting each layer, the scissors are rinsed with pesticide grade acetone for GC Analysis or Methanol for HPLC Analysis. Each cut sample is placed in a labeled culture tube. On 80% of the samples, only the knit layer was cut out and saved.

Fabric samples were extracted according to the following:

Extraction Procedure: For GC Analysis. The pesticide was extracted from the samples by introducing 50 ml of Pesticide Grade Hexane by Repipet® into the culture tube and then shaken for 30 minutes with a Burell wrist-action shaker. The hexane is decanted and an additional 50 ml of hexane is added. The tube is shaken again for 30 minutes. The hexane decanted and combined with the first 50 ml extraction in 125 ml Quar-Pack bottles. An aliquot of this was then placed in a labeled glass vial with a teflon lined cap. The vials are then delivered to be analyzed by gas chromatography.

Extraction Procedure: For HPLC Analysis. The pesticide was extracted from the samples by introducing 25 ml of HPLC grade Methanol by Repipet® into the culture tube and then shaken for 30 minutes with a Burell wrist-action shaker set on maximum shake. The Methanol was decanted into a labeled glass vial with a teflon lined cap. Another portion was decanted into a labeled HPLC auto sampler vial. The auto sampler vials are delivered for analysis by HPLC.

If storage is necessary before analysis, the samples are stored in flammable storage approved freezers which maintain a temperature of -8 C or below. Samples are kept frozen and removed only long enough to be transferred to auto sampler vials or tube catalogs.

Analysis of Extracts

The pesticide extracts were analyzed by gas-liquid chromatography (see Appendix B). Pesticide standards were injected at intervals for calibration curve calculation. Fabric blanks were preextracted to assure that there were no interfering compounds. The procedures for analysis were according to SOP.

Data Analysis, Validation, and Reporting

The collector layer was extracted and the extract analyzed to determine the amount of g/cm^2. Mean values of 5 replications of each fabric sample were used to calculate a mean exposure level for each fabric under investigation. In the design of the study 10% of the fabric assemblies were analyzed by cutting and extracting all 3 layers of the assembly (see Sampling Diagrams, Appendix C). This enabled a verification of the quantity being delivered to the total assembly.

In analyzing the data, the mean values were examined to determine if they fell within a 90% confidence limit for each run. If the data was outside the limit, it was considered to be an outlier and the identified sample was reanalyzed. If the reanalyzed data was found to be outside the limits, the sample was considered an outlier and dropped from the data analysis.

SEWING PROCEDURES FOR SEAMS AND ZIPPERS

I. SEAMS

A. MATERIALS FOR OVERLOCK SEAMS

THREAD: Mercerized cotton covered polyester
MACHINE: Singer® Overlock Professional #10 UJ 13
NEEDLE: 2053
SEAM: 504 stitch (Hudson, 1988)
STITCH: 10 stitches/inch

PROCEDURES FOR SEWING

OVERLOCK INSIDE SEAM

With right sides of fabric together sew a 504 stitch

OVERLOCK OUTSIDE SEAM

With wrong sides of fabric together sew a 504 stitch

B. MATERIALS FOR PLAIN, FLATFELL, BOUND, SEAMS

THREAD: 100% polyester
MACHINE: Singer® Model #28/108
NEEDLE: #80/11
SEAM: 301 stitch (Hudson, 1988)
STITCH: 10 stitches/inch

PROCEDURES FOR SEWING

PLAIN

With right sides together sew a 301 stitch with a 5/8 inch seam allowance

FLATFELL

1) With wrong sides together sew a 301 stitch with 5/8 inch seam allowance
2) Press seam open then to one side
3) Trim inner seam allowance to 1/8"
4) Press under 1/4" on outer seam allowance
5) Stitch this folded edge to garment

BOUND

1) With wrong sides together sew a 301 stitch with 5/8" seam allowance
2) Trim seam allowance to 1/4"
3) Bind seam allowance with self fabric; for denim use Wrights® extra wide 100% cotton double fold bias tape.
4) Self fabric binding--made of 1" strip of self fabric which has each end pressed under 1/4"

II. ZIPPERS

A. MATERIALS FOR ALL ZIPPERS

THREAD:	100% polyester
MACHINE:	Singer® Model #28/108
NEEDLE:	#80/11
SEAM:	301 stitch (Hudson, 1988)
STITCH:	10 stitches/inch

B. PROCEDURE FOR SEWING ZIPPERS

OPEN METAL AND NYLON ZIPPERS

1) Place zipper directly on top of right side of fabric. With zipper foot stitch a 301 stitch down one edge of zipper tape across bottom and up other edge of tape.
2) Slit the fabric directly behind the zipper--make the slit in the lengthwise direction of the zipper coils and center the slit between the two stitching lines.

CENTERED ZIPPER

1) Place right sides of fabric together sew a 301 stitch with machine basting allowing for 5/8" seam allowance.
2) Press seam open, center zipper on seam side facing seam.
3) Stitch down one edge zipper tape across bottom and up other edge of tape.
4) Pull out basting stitch on right side of fabric.

EXPERIMENTAL LAPPED ZIPPER

1) Press under 5/8" on one side fabric.

2) Stitch with a 301 stitch this pressed edge to right side of zipper tape with zipper foot on right side of zipper.
3) Place a 3" wide and 1" wide piece fabric with right sides together. The 3" wide piece on top and left edges together.
4) Place the edges of fabric over unsewn left side of zipper tape. The bulk of fabric pieces will overlap right side of zipper.
5) Sew along unsewn left edge of zipper tape through both fabric and tape with a 301 stitch and zipper foot.
6) Fold back the top 3" wide piece fabric.
7) Place a double stick tape along inner or under edge of overlapping 2" wide fabric to seal zipper closure.

TRADITIONAL LAPPED ZIPPER

1) With right sides together of two 3" pieces of fabric sew a 301 stitch.
2) Press open seam and position zipper face down on right side of right 3" piece, the facing.
3) Align zipper along seam and sew a 301 stitch with zipper foot on left side of zipper tape.
4) Turn facing inside along seam line.
5) Fold a 3/4" fold in a piece of fabric. Make it so have a 1.5" fabric width with a 3/4" width fold and then a 3" width of fabric coming out of tip fold.
6) Fit other edge, right side of zipper, so fold line meets right side of zipper coils; and the 1.5" fabric (under the fold) is under the zipper and the 3" fabric (top side fold) is to the right of the zipper.
7) Sew a 301 stitch with zipper foot along right edge of front of zipper through fabric fold and zipper tape.

APPENDIX B

HIGH PERFORMANCE LIQUID CHROMATOGRAPH CONDITIONS

Dicofol

Column:Waters RCM 100 equipped with 8 mm diameter, 100 mm long Nova-pak C-18 radial compression column

Packing: Nova-pak C-18. End capped, C_{18} alkyl bonded silica, four micrometer diameter spherical particles

Mobile Phase: 75% acetonitrile/25% water; HPLC grade (Burdick & Jackson)

Detector: Waters 490 UV detector at 230 nm

Terrazole®

Column: Waters RCM 100 equipped with 8 mm diameter, 100 mm long Nova-pak C-18 radial compression column.

Packing: Nova-pak C-18. End capped, C_{18} alkyl bonded silica, four micrometer diameter spherical particles.

Mobile Phase: 70% acetonitrile/30% water; HPLC grade (Burdick & Jackson)

Detector: Waters 490 UV detector at 230 nm

GAS CHROMATOGRAPH CONDITIONS

Captan

Column Packing: 4% SE 30 and 6% SP-2401 on a 6 ft. x 2 mm x 120 ft Glass supelcoport

Temperatures:
Injection port - 240°C
Oven - 200°C
Detector - 300°C

Chlorobenzilate

Column Packing: Varian 6000, Fused Silica column, 30 meters in length, open ended, 0.53 mm inside diameter, film thickness 1.5 microns, film - DB1

Temperatures:	Injection port	- 230°C
	Oven	- 210°C isothermic
	Detector	- 270°C
Carrier Gas:	Nitrogen at 20 ml/min	
Detector:	ECD	

Dicofol

Column Packing: Varian 3700, Glass column height of 1.8 m, 2 mm inside diameter, packing 3% SP-2100 on 11-120 supelcoport.

Temperatures:	Injection port	- 210°C
	Oven	- 195°C
	Detector	- 300°C
Carrier Gas:	Nitrogen at 52 ml/min	
Detector:	ECD	

Ethion

Column Packing: Hewlitt-Packard 5730A Fused Silica column 15 meters in height, open ended, 0.53 mm inside diameter, film thickness 1.5 microns, film - DB1 3% SP2100 on a 6 ft x 4 mm x 120 ft. Glass supelcoport

Temperatures:	Injection port	- 250°C
	Oven	- 185°C isothermic
Detector		- 250°C
Carrier Gas:	Nitrogen at 20 ml/min	
Detector:	ECD	

Methyl Parathion

Column Packing: 1.58% SP 2250 and 1.95% SP 2401 on a 6 ft. x 4 mm x 120 ft Glass supelcoport

Temperatures:	Injection port	- 220°C
	Oven	- 200°C
	Detector	- 270°C

APPENDIX C

QUALITY ASSURANCE

Preparation of Standard

Purified EPA pesticides are removed from a desiccated container stored in the freezer at -8°C and allowed to warm up to room temperature. The pesticides are weighed into an appropriate container on a calibrated and checked analytical balance. Initially 10 mg's of pesticide are weighed out using the following formula:

amount desired (10 mg)Pesticide % purity = weight of standard

This amount of pesticide was then diluted to a volume of 10 ml in a volumetric flask being sure to rinse all pesticide out of weighing container without going over the specified volume. The resulting standard has a concentration of 1000 μ g/ml. The rest of the standards are prepared by dilution in class A volumetric glassware.

- 10 μg/ml: 1 ml of 1000 μg/ml std. diluted to 100 ml.
- 5 μg/ml: 1 ml of 1000 μg/ml std. diluted to 100 ml.
- 1 μg/ml: 10 ml of 10 μg/ml std. diluted to 100 ml.
- 0.1 μg/ml: 1 ml of 10 μg/ml std. diluted to 100 ml.
- 0.02 μg/ml: 1 ml of 1.0 μg/ml std. diluted to 50 ml.

These standards are mixed well by inverting before further dilutions and before transferring to 100 ml bottles with teflon lined caps.

Precision

Precision for this project was achieved through standard fortification and subsequent extraction of each fabric used in the study. Each laboratory technician fortified at least three fabric samples with an 8 nanograms sample of the appropriate pesticide and performed the extraction procedure. The evaluation of extraction efficiencies provided an estimate of the consistency of each technician in the established extraction procedure.

Extraction Efficiency: Three culture tubes are prepared for each person who is performing the extractions on a pesticide. A 1" x 3" sample of knit fabric is placed in each culture tube and the tubes are labeled. One milliliter of a 10 μg/ml solution of the pesticide is pipeted onto two of the fabrics in the culture tubes. One tube is left as a blank. The tubes are left open so the samples may air dry for one hour. The person for whom the extraction efficiencies are prepared then proceeds to extract the samples by introducing 25 ml of HPLC grade Methanol by Repipet® into the culture tube. The tube is capped with a teflon lined lid and shaken for 30 minutes on maximum with a

Burell wrist-action shaker. The Methanol was decanted into a labeled glass vial with a teflon lined cap. Another portion was decanted into a labeled HPLC auto sampler vial. The extraction efficiency samples are mixed in during the extraction of other samples of the same pesticide.

When necessary 1" x 3" samples of the test fabrics are treated in the same manner and extraction efficiencies determined (Tables 52-53).

Table 52. TERRAZOLE® EXTRACTION EFFICIENCY

Theoretical Sample	Actual Concentration ng/ml	Measured Concentration ng/ml	Percent Recovery
TTN1TTA1	0	0	
TTN1TTA2	0.4	0.438	110
TTN1TTA3	0.4	0.366	92
			101 Mean
			12.7 S. Dev.
TTN2TTA4	0	0	
TTN2TTB1	0.4	0.397	99
TTN2TTB2A	0.4	0.385	96.3
TTN2TTB2B	0.4	0.392	98
			97.8 Mean
			1.4 S. Dev.
TTN1KTA1	0	0	
TTN2KTB2	0.4	0.437	109.3
TTN3KTB3	0.4	0.397	99.3
			104.3 Mean
			7.1 S. Dev.

Table 53. DICOFOL EXTRACTION EFFICIENCY

Sample	Actual Concentration ng/ml	Measured Concentration ng/ml	Percent Recovery
DDNTDA1	0	0	
DDN1TDA2	0.4	1.231	307.8
DDN1TDA3	0.4	0.640	160
			233.9 Mean
			104.5 S. Dev.
DDN2TDA4	0	0	
DDN2TDB1A	0.4	0.426	106.5
DDN2TDB1B	0.4	0.426	106.5
DDN2TDB2	0.4	0.4	100
			104.3 Mean
			3.8 S. Dev.
DDN3TDB3	0	0	
DDN3TDB4	0.4	0.34	85
DDN3TDC1	0.4	0.38	95
			90 Mean
			7.1 S. Dev.
DDN4TDC2	0	0.01	
DDN4TDC3	0.4	0.37	93
DDN4TDC4	0.4	0.39	98
			95.5 Mean
			3.5 S. Dev.
DDN1KDA1	0	0.01	
VVN3KDB2	0	0	
DDN3KDB3	0.4	0.38	95
DDN2KDB2	0.4	0.40	100
VVN1KDA1	0.4	0.386	96.5
VVN2KDB1A	0.4	0.393	98
VVN2KDB1B	0.4	0.401	100.3
			98 Mean
			2.3 S. Dev.

Accuracy

Inherent in the above routine is the implication of accuracy. Accuracy for the study was assured by the supervised adherence to established laboratory standard operating procedures. Each technician was checked at least one time per month for strict adherence to the procedures. Ten percent of the total number of samples were reinjected and indicated as shown in Table 53.

Table 54. DICOFOL REINJECTION DATA-STANDARDS

Specimen	Standard Concentration	AreaCounts
NOVA92	10.0 ppm	1,541,017
NOVA93		1,572,968
NOVA117	10.0 ppm	1,535,124
NOVA118		1,533,883
NOVA128	10.0 ppm	1,728,484
NOVA129		1,725,079
NOVA160	10.0 ppm	1,668,146
NOVA161		1,696,425
NOVA188	10.0 ppm	1,734,139
NOVA189		1,732,714
NOVA198	10.0 ppm	1,512,328
NOVA199		1,511,664
NOVA206	10.0 ppm	1,616,053
NOVA207		1,655,490
NOVA214	10.0 ppm	1,730,269
NOVA215		1,715,414
NOVA222	10.0 ppm	1,716,768
NOVA226		1,719,151
NOVA230	10.0 ppm	1,781,037
NOVA231		1,834,517
NOVA238	10.0 ppm	1,712,269
NOVA239		1,714,165
NOVA240		1,861,470
NOVA246	10.0 ppm	1,710,310
NOVA247		1,751,106
NOVA267	10.0 ppm	1,780,476
NOVA268		1,786,270
NOVA275	10.0 ppm	1,688,274
NOVA276		1,676,265
NOVA283	10.0 ppm	1,759,061
NOVA284		1,760,103
NOVA289	10.0 ppm	1,757,333
NOVA290		1,755,650
NOVA309	10.0 ppm	1,741,207
NOVA310		1,739,660
NOVA317	10.0 ppm	1,741,217
NOVA318		1,746,994

Table 54. (continued)

Specimen	Standard Concentration	AreaCounts
NOVA404	10.0 ppm	1,310,788
NOVA405		1,316,545
NOVA433	10.0 ppm	1,697,820
NOVA434		1,693,554
CCSTD3	10.0 ppm	1,269,809
CCSTD4		1,270,835
NOVA380	10.0 ppm	1,345,708
NOVA381		1,345,135
NOVA452	10.0 ppm	1,706,108
NOVA453		1,705,748
NOVA460	10.0 ppm	1,715,899
NOVA461		1,715,294
NOVA468	10.0 ppm	1,698,245
NOVA469		1,704,614
NOVA476	10.0 ppm	1,701,275
NOVA477		1,695,533
NOVA488	10.0 ppm	1,708,152
NOVA489		1,705,507
NOVA496	10.0 ppm	1,696,075
NOVA497		1,702,686
UUSTD1	10.0 ppm	1,328,847
UUSTD2		1,330,202
VVSTD1	10.0 ppm	1,320,743
VVSTD2		1,318,032
NOVA94	1.0 ppm	151,031
NOVA95		152,557
NOVA119	1.0 ppm	154,366
NOVA120		153,507
NOVA130	1.0 ppm	163,745
NOVA131		166,318
NOVA162	1.0 ppm	168,058
NOVA163		167,758
NOVA180	1.0 ppm	181,521
NOVA181		182,050
NOVA190	1.0 ppm	173,271
NOVA191		175,585
NOVA200	1.0 ppm	160,181
NOVA201		161,605
NOVA208	1.0 ppm	162,989
NOVA209		162,122

Table 54. (continued)

Specimen	Standard Concentration	AreaCounts
NOVA216	1.0 ppm	168,067
NOVA217		172,829
NOVA223	1.0 ppm	179,699
NOVA227		179,737
NOVA232	1.0 ppm	179,273
NOVA233		179,901
NOVA248	1.0 ppm	174,467
NOVA249		175,289
NOVA269	1.0 ppm	175,827
NOVA270		176,804
NOVA277	1.0 ppm	171,944
NOVA278		172,247
NOVA285	1.0 ppm	179,017
NOVA286		179,527
NOVA291	1.0 ppm	179,174
NOVA292		181,800
NOVA311	1.0 ppm	172,820
NOVA312		169,738
NOVA319	1.0 ppm	164,067
NOVA320		166,402
NOVA406	1.0 ppm	128,909
NOVA407		129,119
NOVA435	1.0 ppm	170,145
NOVA436		170,054
CCSTD5	1.0 ppm	126,354
CCSTD6		126,097
NOVA382	1.0 ppm	137,687
NOVA383		136,056
NOVA454	1.0 ppm	167,530
NOVA455		167,825
NOVA462	1.0 ppm	168,643
NOVA463		168,349
NOVA470	1.0 ppm	170,421
NOVA471		170,170
NOVA478	1.0 ppm	166,916
NOVA479		166,481
NOVA490	1.0 ppm	172,408
NOVA491		172,790
NOVA498	1.0 ppm	169,029
NOVA499		168,906

Table 54. (continued)

Specimen	Standard Concentration	AreaCounts
UUSTD3	1.0 ppm	134,600
UUSDT4		147,703
VVSTD3	1.0 ppm	132,221
VVSTD4		131,650
NOVA96	0.2 ppm	31,435
NOVA97		28,542
NOVA98		30,793
NOVA67	0.1 ppm	9,185
NOVA68		9,185
NOVA121	0.1 ppm	15,150
NOVA122		16,153
NOVA123		16,566
NOVA132	0.1 ppm	16,819
NOVA133		16,487
NOVA134		16,475
NOVA164	0.1 ppm	16,250
NOVA165		16,297
NOVA183	0.1 ppm	18,586
NOVA184		17,645
NOVA192	0.1 ppm	16,824
NOVA193		17,122
NOVA194		20,091
NOVA202	0.1 ppm	16,450
NOVA203		17,137
NOVA210	0.1 ppm	15,329
NOVA211		16,026
NOVA218	0.1 ppm	16,220
NOVA219		16,081
NOVA224	0.1 ppm	23,525
NOVA228		23,014
NOVA234	0.1 ppm	20,651
NOVA235		23,404
NOVA271	0.1 ppm	19,077
NOVA272		18,510
NOVA279	0.1 ppm	19,353
NOVA280		22,899
NOVA313	0.1 ppm	14,255
NOVA314		15,247
NOVA321	0.1 ppm	17,124
NOVA322		14,669

Table 54. (continued)

Specimen	Standard Concentration	AreaCounts
NOVA408	0.1 ppm	13,102
NOVA409		12,801
NOVA437	0.1 ppm	17,767
NOVA438		8,444
CCSTD7	0.1 ppm	11,848
CCSTD8		12,056
NOVA384	0.1 ppm	14,742
NOVA385		14,368
NOVA456	0.1 ppm	16,975
NOVA457		15,245
NOVA464	0.1 ppm	15,305
NOVA465		15,204
NOVA472	0.1 ppm	18,670
NOVA473		18,238
NOVA480	0.1 ppm	15,756
NOVA481		15,159
NOVA492	0.1 ppm	19,394
NOVA493		19,150
NOVA500	0.1 ppm	15,282
NOVA501		15,529
UUSTD5	0.1 ppm	13,237
UUSTD6		13,444
VVSTD5	0.1 ppm	13,776
VVSTD6		13,622
NOVA99	0.02 ppm	2,782
NOVA100		2,453
NOVA102		2,850
NOVA124	0.02 ppm	2,431
NOVA126		2,395
NOVA127		3,391
NOVA135	0.02 ppm	2,974
NOVA136		3,034
NOVA137		3,029
NOVA138		2,955
NOVA166	0.02 ppm	3,068
NOVA167		2,946
NOVA185	0.02 ppm	2,136
NOVA186		2,987
NOVA187		3,017
NOVA204	0.02 ppm	5,412

Table 54 (continued)

Specimen	Standard Concentration	AreaCounts
NOVA205		4,381
NOVA220	0.02 ppm	2,392
NOVA221		2,329
NOVA236	0.02 ppm	2,656
NOVA237		4,056
NOVA273	0.02 ppm	2,832
NOVA274		2,922
NOVA315	0.02 ppm	2,904
NOVA316		3,468
NOVA323	0.02 ppm	3,356
NOVA324		3,993
NOVA410	0.02 ppm	3,309
NOVA411		3,289
CCSTD9	0.02 ppm	2,366
CCSTD10		2,478
NOVA386	0.02 ppm	3,989
NOVA387		6,719
NOVA458	0.02 ppm	3,330
NOVA459		3,478
NOVA466	0.02 ppm	3,326
NOVA467		4,165
NOVA474	.02 ppm	3,518
NOVA475		3,699
NOVA482	0.02 ppm	3,529
NOVA483		3,483
NOVA494	0.02 ppm	3,565
NOVA495		3,398
NOVA502	0.02 ppm	2,737
NOVA503		3,557
UUSTD7	0.02 ppm	2,726
UUSTD8		2,697

Completeness

This project was designed with relatively simple methodology and we did not anticipate many errors (wrong date, dropped samples, etc.) and therefore 98% completeness was obtained for the Woven Fabric Study (see Table 55) and 100% completeness for the Nonwoven Studies (see Table 56) and for seams and zipper study (see Tables 57-58).

Table 55. TOTAL NUMBER OF SAMPLES WOVEN

FABRIC ID		W3	W4	W5	W6	W1	W2	W7	W8	W9	W10	W11
Chlorobenzilate												
	Foil	1	1	1	1	1	1	1	1	1	1	1
	Knit	5	5	5	5	5	5	5	5	5	5	5
	Top	1	1	1	1	1	1	1	1	1	1	1
Dicofol	Foil	1	1	1	1	1	1	1	1	1	1	1
	Knit	5	5	5	5	5	5	5	5	5	5	5
	Top	.	1	.	1	.	1	.	1	1	1	.
Ethion	Foil	1	1	1	1	1	1	1	1	1	1	1
	Knit	5	5	5	5	5	5	5	4	5	5	5
	Top	1	.	1	1	1	1	1	1	1	1	1
All		20	20	20	21	20	21	20	20	21	21	20

FABRIC ID		W12	W13	W14	W15	W16	W25	W23	N1	N7	ALL
Chlorobenzilate											
	Foil	1	1	1	1	1	1	1	1	1	20
	Knit	5	5	5	5	5	5	5	5	5	100
	Top1	1	1	1	1	1	1	1	1	1	20
Dicofol	Foil1	1	1	1	1	1	1	1	1	1	20
	Knit	5	.	5	5	5	5	5	5	5	100
	Top	1	.	1	.	1	1	1	1	1	13
Ethion	Foil	1	1	1	1	1	1	1	1	1	20
	Knit	5	5	5	5	5	5	5	5	5	99
	Top1	1	1	1	1	1	1	1	1	1	19
All		21	20	21	20	21	21	21	21	21	411

Table 56. TOTAL NUMBER OF SAMPLES NONWOVEN

Fabric ID Pesticide	Layer ID	N15	N16a	N16b	N18	N2	W23	N17	N3	N79	W25	N1	N4	All
Chlorobenzilate														
	Foil	1	1	1	1	1	1	1	1	1	1	1	1	12
	Knit	5	5	5	5	5	5	5	5	5	5	5	5	60
	Top	1	1	1	1	1	1	1	1	1	1	1	1	12
Dicofol	Foil	1	1	1	1	1	1	1	1	1	1	1	1	12
	Knit	5	5	5	5	5	5	5	5	5	5	5	5	60
	Top	1	1	1	1	1	1	1	1	1	1	1	1	12
Ethion	Foil	1	1	1	1	1	1	1	1	1	1	1	1	12
	Knit	5	5	5	5	5	5	5	5	5	5	5	5	60
	Top	1	1	1	1	1	1	1	1	1	1	1	1	12
All		21	21	21	21	21	21	21	21	21	21	21	21	252

Table 57. TOTAL NUMBER OF SAMPLES SEAMS

Fabric ID		1	2	3	4	5	6	7	8	9	10	11	12
	Foil	1	1	1	1	1	1	1	1	1	1	1	1
Dicofol	Knit	5	5	5	5	5	5	5	5	5	5	5	5
	Top	1	1	1	1	1	1	1	1	1	1	1	1
	Foil	1	-	-	1	1	1	1	-	-	1	1	1
Terrazole®	Knit	5	-	-	5	5	5	5	-	-	5	5	5
	Top	1	-	-	1	1	1	1	-	-	1	1	1
All		14	7	7	14	14	14	14	7	7	14	14	14

- indicates seams not used in Terrazole® study

Fabric ID		13	14	15	16	17	18	19	20	21	22	23	24	All
	Foil	1	1	1	1	1	1	1	1	1	1	1	1	24
Dicofol	Knit	5	5	5	5	5	5	5	5	5	5	5	5	120
	Top	1	1	1	1	1	1	1	1	1	1	1	1	24
	Foil	-	-	-	-	-	-	-	-	-	-	-	-	8
Terrazole®	Knit	-	-	-	-	-	-	-	-	-	-	-	-	40
	Top	-	-	-	-	-	-	-	-	-	-	-	-	8
All		7	7	7	7	7	7	7	7	7	7	7	7	224

- indicates seams not used in Terrazole® study

Table 58. TOTAL NUMBER OF SAMPLES ZIPPER CLOSURES

Pesticide	Layer ID	1	2	3	4	5	Al
	Foil	4	4	4	3	4	19
Dicofol	Knit	16	16	16	16	16	80
	Top	4	4	4	4	4	19
All		24	24	24	24	24	118

Sample Custody

Sample custody was tightly controlled. Two bound notebooks were kept: one for the spraying operation and one for laboratory analysis. The spray test notebook included: pre-laundry of fabric details, date, fabric cutting and assembly preparation, pesticide preparation and order of exposure time, drying time, sample cutting and release of sample for analysis dates.

The laboratory notebook was used to trace each run through the laboratory procedure including calculations. Information to be recorded included: date removed from storage, date extracted, extraction storage date and location, date analyzed, date restored and reanalysis dates.

As GC analysis was not conducted in The University of Tennessee Pesticide laboratory, a sample of each extract was prepared for shipping to the analytical labs. The remaining sample extracts were stored in the UT laboratory. This enabled the control of any lost sample by the analytical laboratories.

INTERLABORATORY EVALUATION OF PESTICIDE ANALYTICAL METHODS

The purpose of this study was to demonstrate the accuracy and precision of high performance liquid chromatography (HPLC) methods for pesticide trace analysis and establish that HPLC results are comparable to pesticide analyses by gas chromatography (GC).

Ten specimens of Dicofol in methanol were prepared for analysis. The specimens are described in Table 59. Specimen 1LT1 was the pure HPLC grade methanol used to make standard pesticide solutions. Specimens 1LT2, 1LT4 and 1LT10 were dicofol standard solutions made from the pure pesticide standard supplied by EPA. Specimen 1LT6 was a methanol extract of an uncontaminated knit fabric. Specimens 1LT5 and 1LT8 were a methanol extract of a knit fabric contaminated with ten micrograms of dicofol standard. Specimens 1LT3, 1lT6 and 1LT9 were methanol extracts of knit fabrics contaminated by usual spray test procedures using a Dicofol field spray mix.

The ten test specimens were analyzed independently by three laboratories. The test key was not revealed to participants until all data were submitted. The specimens were analyzed by gas chromatography (GC) in The University of Tennessee, Civil Engineering Department (Sharon Hale)

Table 59. EPA PESTICIDE ANALYSIS-INTERLAB SPECIMEN I.D.

Specimen	Identification
1LT1	Solvent blank (pure methanol)
1LT2	.10 ppm dicofol standard solution
1LT3	Dicofol unknown from EPA study (ON3KDA5) (methanol extract of spray tested fabric)
1LT4	1.0 ppm dicofol standard solution
1LT5	Extraction efficiency test sample (YN1KDB1) (methanol extract of fabric spiked with dicofol standard. 0.4 ppm = 100% extraction)
1LT6	Fabric blank (methanol extract of uncontaminated knit fabric)
1LT7	Dicofol unknown from EPA study (ON3KDB4)
1LT8	Extraction efficiency test sample (YN1KDB1) (1LT8 is the same as 1LT5)
1LT9	Dicofol unknown from EPA study (NN3KDA1)
1LT10	.020 ppm dicofol standard solution

and The University of Florida, Citrus Research and Education Center (Herbert Nigg). The same specimens were analyzed by HPLC in The University of Tennessee, Textiles, Merchandising and Design Department (John Crouse). The results were analyzed for precision, accuracy and consistency. The precision was determined by subtracting the standard deviation from the mean value and dividing the difference by the mean value. The accuracy of the method was determined by the ratio of test results to the nominal concentration values.

Table 60. EPA PESTICIDE ANALYSIS-INTERLAB TEST U.T. HPLC

Specimen	run 1	run 2	run 3	run 4	Mean	Std. Dev.	Precision	Accuracy
1LT1	ND	ND	ND	ND	ND	---	---	---
1LT2	.093	.098	.098	0.99	0.97	.003	97%	97%
1LT3	.376	.363	.365	.370	.368	.006	98%	---
1LT4	.976	.981	.857	.979	.938	.070	92%	94%
1LT5	.404	.403	.383	.391	.395	.010	97%	---
1LT6	ND	ND	ND	ND	ND	---	---	---
1LT7	.026	.026	.026	.025	.026	.0004	99%	---
1LT8	.387	.388	.411	.414	.400	.014	97%	---
1LT9	1.45	1.37	1.36	1.36	1.39	.046	97%	---
1LT10	.016	.014	.019	.015	.016	.002	88%	80%

The results of four HPLC analyses are presented in Table 60. The results of two GC analyses are presented in Table 61. Dr. Nigg cited technical difficulty and did not report data for this study.

The HPLC data show the precision and accuracy of the HPLC technique. The standard deviations are low. The average precision index was 95.6%. The determinations of the Dicofol

Table 61. EPA PESTICIDE ANALYSIS-INTERLAB TEST U.T. GC

Specimen	run 1	run 2	Mean	Std. Dev.	Precision	Accuracy
1LT1	ND	ND	ND	---	---	---
1LT2	.083	.083	.083	.000	100%	83%
1LT3	.318	.333	.326	.011	97%	---
1LT4	.881	.901	.891	.014	98%	89%
1LT5	.343	.357	.350	.010	97%	---
1LT6	ND	ND	ND	---	---	---
1LT7	.021	.019	.020	.001	95%	---
1LT8	.383	.425	.404	.030	93%	---
1LT9	1.19	1.21	1.20	.014	99%	---
1LT10	.016	.017	.017	.001	94%	85%

Table 62. SAMPLING DIAGRAM VARIABLES AFFECTING PENETRATION

Fabric ID Block	N13	W23	N2b	Ex1	W21	W22	W25	W24	W26	Ex2	N2a	N1
1	4	2	1	3								
2				2	4	1	3					
3		3					1	2	4			
4	3									4	1	2
5						4	3		1		2	
6		2	3					4				1
7					1	2		3				4
8	3		4		2				1			
9		1		4						2	3	
10			4		3	2				1		
11	2						4		1			3
12			1	2		3				4		
13		4			3			1			4	
14				1					3		2	4
15	4						2	1		3		

standards concentrations were very accurate with the exception of 1LT10. However, the mean value determined by HPLC was very close to the value determined by GC. The inaccuracy may have been due to errors not associated with the chromatography.

The GC data in Table 61 show that the UT GC work is precise and accurate as well. Quantitative comparison of the two methods may be misleading due to the different number of injections performed in the two laboratories. However, the GC data do corroborate at the HPLC results. The generally lower values obtained by GC analysis may be partially explained by the fact that each laboratory prepared calibration standards independently.

HPLC analysis for Dicofol is precise and accurate. The method is reliable and is comparable to the analysis for dicofol by gas chromatography.

Statistical Analysis

To determine the effectiveness of a fabric as a barrier to pesticide penetration, the amount of pesticide which travels through this fabric is considered. This pesticide was collected on layer 2 of the multilayer sample. The data used in the statistical analysis was based on micrograms per square centimeter of the pesticide extracted from the collector layer and analyzed using gas chromatography. The mean of five replications for each fabric/pesticide combination was used. Fabric properties were measured and the mean of three or five replications (depending on the standard test procedure) were used in the statistical analysis (Tables 62-71).

Several statistical procedures were used to complete the analysis. These included Analysis of Variance (ANOVA), Duncan's Multiple Range Test, and Least Squares Analysis of Variance. These statistical procedures were performed using the General Linear Model (GLM) procedure available in the Statistical Analysis System computer program. Null hypotheses were used in this analysis.

The GLM procedure selected for this study used the method of least squares to fit general linear models. GLM handles classification variables such as fabric finish and construction, as well as continuous variables which measure quantities such as spray rating and weight. Thus, GLM can be used for many different analyses.

Analysis of variance was used to determine the relationship between pesticide amount (dependent variable) and fabric (independent variable) for each set. Due to the small amount of pesticide being detected and the indication of heteroscedasticity, log transformations were applied to the dependent variable. For the remainder of the analysis, log transformations were used. The 0.5 level was used to establish significance.

The data was reanalyzed using log transformations and Duncan's Multiple Range Test was used to group the data that showed similar amounts of pesticides. A large percentage of the observations were zero, indicating no penetration had occurred. Data was analyzed including the zero values and then excluding the zero valued to eliminate any downward biasing of the results.

Table 63. SAMPLING DIAGRAM (EFFECT OF SEAMS - DICOFOL)

Fabric ID Block	1	2	3	4	5	6	7	8	9	10	11	12
1	1		2				4					3
2					4		1					
3								4				1
4	2							3				1
5		2							4		3	
6					3				1			
7						3					1	
8										2		
9			1	4						2		
10	3						2					
11		1			4			2				
12			1		4						2	
13				2					1			
14	2	1										3
15									4		2	
16		1									3	
17			2						3			
18								3				
19			2		4	3						
20		1										
21							4					

Fabric ID Block	13	14	15	16	17	18	19	20	21	22	23	24
1												
2	3								2			
3	3								2			
4										4		
5								1				
6				4				2				
7		2						4				
8		3							4	1		
9					3							
10	1									4		
11						3						
12												3
13				3							4	
14		4										
15	3							1				
16		2				4						
17	4			1								
18				1		4		2				
19											1	
20		2	3					4				
21			3		2							

Table 64. SAMPLING DIAGRAM (EVALUATION NONWOVEN FABRICS)

Fabric ID Block	N1	N2	N3	N4	N7	N15	N16A	N16B	N17	N18	W23	W25
1			4*		2				3			1
2				4*		3	1					
3						2	4*	3		1		
4				4		2*			1		3	
5		2	4					3				1
6	4*	3	2				1					
7				3	4*			2			1	
8		3*		2					4		1	
9					3		2			4*		1
10		1	4	3		2						
11	4							1	3		2	
12						4			1*	2		3
13		3						4*		1	2	
14												
15	3				1		2			4		
	2			3	1							4*

* indicates the 20% of the samples that had all three layers analyzed.

Table 65. SAMPLING DIAGRAM (SEAMS -TERRAZOLE®)

Fabric ID Block	1	4	5	6	7	10	11	12
1	3			4	1	2		
2	2	3		1			4	
3	2	4				3		
4	2		4		3		1	
5	3		2			1	4	
6		1	2	3		4		
7			1		4	3		2
8		3	4				1	2
9		4		1	2			3
10				1	3		4	2

Table 66. SAMPLING DIAGRAM (ZIPPERS - DICOFOL)

Fabric ID Block	1z	2z	3z	4z	5z
1	1	2	4		3
2	1	2		3	4
3	1		4	3	2
4		1	2	3	4
5	1	3	4	2	
6	4	2		3	1
7	1	2	4		3
8	2		4	3	1
9		3	1	4	2
10	4	1	2	3	
11	3	4		2	1
12	4		3	2	1
13	2	4	3		1
14	4	2	3	1	
15		4	2	3	1
16	1		3	2	4
17	3	4		2	1
18	1	4	3		2
19	2	1	4	3	
20		2	3	1	4

Table 67. SAMPLING DIAGRAM (PENETRATION - DICOFOL)

Fabric ID Block	N3	N4	N9	N10
1 Pass				
1	A	C	D	B
2	D	B	C	A
3	C	A	B	D
4	B	D	A	C
5	C	D	B	A
2 Passes				
1	A	C	D	B
2	D	B	C	A
3	C	A	B	D
4	B	D	A	C
5	C	D	B	A
3 Passes				
1	A	B	C	D
2	D	A	B	C
3	C	D	A	B
4	B	C	D	A
5	A	B	C	D

Table 68. SAMPLING DIAGRAM (PENETRATION - TERRAZOLE ®)

Fabric ID Block	N3	N4	N9	N10
1 Pass				
1	A	B	C	D
2	D	A	B	C
3			A	B
4	C	D		
5	B	C	D	A
6	A	B	C	D
2 Passes				
1	D	A	B	C
2	C	D	A	B
3	B			A
4		C	D	
5	A	B	C	D
6	D	A	B	C

Table 69. SAMPLING DIAGRAM (FABRICS TERRAZOLE®)

Fabric ID Block	N3	N4	N9	N10
1 Pass				
1	A	B		
2			C	D
3		A	B	
4	D			C
5			A	B
6	C	D		
7	B			A
8		C	D	
9	A	B		
10			C	D
2 Passes				
1			A	B
2	C	D		
3	B			A
4		C	D	
5	A	B		
6			C	D
7		A	B	
8	D			C
9			A	B
10	C	D		

Table 70. SAMPLING DIAGRAM (FABRICS DICOFOL)

Fabric ID Block	N3	N4	N9	N10
1 Pass				
1	B		A	
2		C		D
3	A	B		
4			D	C
5		A		B
6	D		C	
7		B	A	
8	C			D
9	B	A		
10			D	C
2 Passes				
1	C	A	B	D
2	B	D	A	C
3	A	C	B	D
4	D	A	B	C
5	B	D	A	C
3 Passes				
1	A	B	C	D
2	D	A	B	C
3			A	B
4	C	D		
5	B	C	D	A
6	A	B	C	D

Table 71. TOTAL CONTAMINATION LEVELS

Total Contamination	(µg/cm^2)	Standard Deviation (µg/cm^2)
Dicofol Capillary Penetration Tests		
One Pass	5.95	1.44
Two Passes	15.93	2.46
Three Passes	20.88	2.89
Dicofol Pressure Penetration Tests		
One Pass	6.78	0.80
Two Passes	13.03	3.41
Three Passes	17.09	2.60
Terrazole® Capillary Penetration Tests		
One Pass	0.6617	0.4222
Two Passes	1.9003	1.2291
Terrazole® Pressure Penetration Tests		
One Pass	2.6394	1.6014
Two Passes	3.7895	2.5556